A STUDY OF ADSORPTION OF BENZENE AND WATER ON MIXED ADSORBENTS OF CARBON AND SILICA GEL

A THESIS

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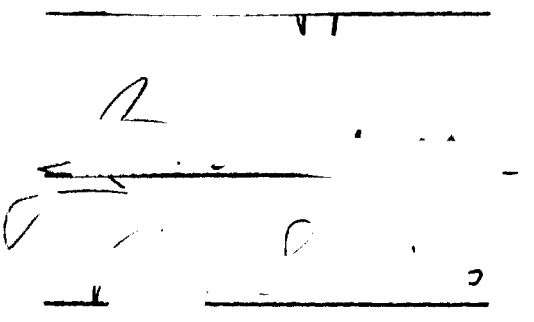
Approved:



Date Approved by Chairman May 27 1952

PREFACE

The statement was made by Brunauer that "The case of mixed adsorbents and mixed adsorbates is of vital interest in chemiadsorption, but nothing of significance has been published on it as yet in the field of physical adsorption."[1] In this work the purpose has been to prepare intimate mixtures of carbon and silica following as nearly as possible the work of Fells and Firth,[2] and of Shilov, Dubinin and Toropov.[3] Both groups found that there existed an optimum composition of carbon and silica for which the amount of material adsorbed reached a maximum. However, there is an apparent contradiction in their work since Fells and Firth found this optimum composition to be in the neighborhood of eighteen per cent carbon, while Shilov, Dubinin and Toropov found the optimum to be between sixty and seventy per cent carbon.

We have attempted to duplicate the work of both of the above groups with the purpose of investigating the

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[1] S. Brunauer, The Adsorption of Gases and Vapors, Vol.I (Princeton: Princeton University Press, 1943) p. 497.

[2] H. H. Fells and J. B. Firth, J. Soc. Chem. Ind., 41, 39T (1927).

[3] N. Shilov, M. Dubinin, and S. Toropov, Kolloid Z., 49, 120 (1929).

cause of the existence of these maxima in adsorptive capacity.

For the suggestion of this problem and for the aid, advice given, and the patience shown, I wish to express my sincerest thanks to Dr. R. F. Sessions. I would like also to express my gratitude to members of the Department of Chemistry and of the Department of Chemical Engineering who have graciously made needed equipment available as the need presented itself.

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ABSTRACT

Reports have been made by several investigators (i.e., Fells and Firth; Shilov, Dubinin, and Toropov; and Chowdhury, et al.) of intimate mixtures of two or more adsorbents showing activities superior to that of any one of the single adsorbents used. In this thesis intimate mixtures of silica with charcoal from cane sugar and from birch wood were prepared, and the effect of the carbon content on the adsorption capacities of the adsorbents for benzene and water vapors were studied. The adsorption capacities were determined by both a static and a dynamic method. Both methods gave essentially the same results, but the dynamic method was the more rapid. The break point, the point at which the first trace of adsorbate was found in the effluent air stream, was also established.

The results confirm the work of none of the above investigators, but seems to support the work of Lachs, who found that mixed adsorbents adsorb in proportion to the amount of each single adsorbent present. The adsorbents prepared in this thesis from silica and charcoal from cane sugar show essentially the same capacity as sugar charcoal until the composition reaches fifty per cent silica. Between 50 and 100 per cent silica, the adsorption capacity increases

to that of silica gel. The capacities of the adsorbents prepared from silica and birch wood charcoal increase directly with the silica content until a composition of about 55 per cent silica is reached, then the capacity drops off sharply. In neither of the above series of adsorbents does the adsorbent show a capacity greater than straight silica gel.

The break point capacities do not parallel the saturation capacities, but instead show a minimum between forty and fifty per cent carbon.

The adsorbents were all analyzed, and it was found that the water content of the analyzed samples increased directly with the carbon content of the samples. This is contrary to what one would expect from the relative activities of silica and charcoal for water. The water content decreased with the temperature of activation of the adsorbents. The hydrogen content of the analyzed adsorbents was found to increase both with the carbon content and with the temperature of activation.

The mixed adsorbents from silica and charcoal from cane sugar show about the same capacities when activated at 300°C as they do when activated at 600°C.

CHAPTER I

INTRODUCTION

During the past two decades much work has been done in the field of surface chemistry and in the study of adsorption phenomena, but most of this work has been limited to systems having only one adsorbent and one adsorbate. The study of mixed adsorption in the field of physical adsorption has not been undertaken to any great extent.[1]

A study of mixed adsorption may be divided into three parts as follows:[2]

(1) A single adsorbent and a mixture of gases. This is the most important type of mixed physical adsorption from the point of view of materials studied thus far.

(2) One adsorbate and a mixture of adsorbents. So far very little work has been done in this field.

(3) Mixed adsorbents and mixed adsorbates. This phenomena occurs frequently in practical adsorption processes. Many catalytic reac-

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[1] S. Brunauer, The Adsorption of Gases and Vapors, Vol. I (Princeton: University Press, 1943) p. 497.

[2] Ibid., p. 474.

tions belong to this group. Catalytic reactions, however, belong in the field of chemiadsorption, a field with which this research is only indirectly concerned.

The Problem.— Several investigators have found that adsorbents composed of varying proportions of carbon and silica gel, when intimately mixed, show increased adsorption over the single adsorbents, and reach a maximum for certain optimum compositions. However, they disagree widely on the composition of the adsorbents at these maxima.

The purpose of this research is (1) to attempt to duplicate the work of these investigators, (2) to determine the surface areas of the adsorbents at the peaks which it is expected will be found, and (3) to correlate the change in adsorption capacity of the adsorbents with the change in surface area or with the change in surface energy.

CHAPTER II

REVIEW OF THE LITERATURE

As was mentioned in Chapter I, comparatively little work has been done on the study of physical adsorption on mixed adsorbents. However, in work that has been done, it has been noticed that in many cases the amount of material adsorbed is different from that expected if each of the adsorbents had acted independently. In some cases, the amount of material adsorbed has been found to be greater than that adsorbed by an equal weight of either of the adsorbents alone.

Lachs, the first investigator to report studies of adsorption on mixtures of adsorbents, found that mechanical mixtures of any two adsorbents (charcoal, wood, clay, meerschaum, and quartz), when suspended in solutions of inorganic acids, bases, and acetone, adsorbed a quantity equal to the sum of the quantities adsorbed by each adsorbent when present alone. However, when the solutions were very dilute, the quantity adsorbed was less than this sum.[1]

Of all the many adsorbents that have been investigated, probably charcoal and silica gel are the two which have re-

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[1] H. Lachs, Z. Physik Chem., 91, 170 (1916).

ceived the most intensive study. Mixtures of each of these with other substances has also been studied to some degree.

Reyerson and Swearington,[2] during their investigations of the adsorption of various gases on silica gel in the presence of very finely divided metals, found that the gases were better adsorbed on gels containing the metals than they were by the silica gel alone. The amount of metal present seems to have little effect since it was later found that increase in metallization did not cause any great increase in adsorption.[3]

The effect of the presence of various metallic oxides on the adsorption capacity of silica gel has been studied by Holmes and Anderson[4] and by Markov.[5] Holmes and Anderson prepared an intimate mixture of silica and ferric oxide and found that the gel obtained had better adsorption for benzene than the silica gel alone. Markov has extended this work by investigating the effect of other metal oxides on the adsorption capacity of silica gel for benzene.

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[2]L. H. Reyerson and L. E. Swearington, J. Phys. Chem., 31, 88 (1927).

[3]L. H. Reyerson and M. R. Cines, J. Phys. Chem., 46, 1060 (1942).

[4]H. N. Holmes and J. A. Anderson, Ind. Eng. Chem., 17, 280 (1925).

[5]V. K. Markov, Ukrain. Khem. Zhur., 8, No. 1, Wiss Teil 16 (1933) in Chemical Abstracts, 28, 2968-9 (1934).

While searching for an adsorbent to use as a desulfurising agent in the petroleum industry, Chowdhury and Bogchi[6] prepared mixtures of aluminia with silica gel and with activated charcoal. An intimate mixture of silica gel and alumina, prepared by suspending silica gel in a solution of aluminum sulfate and precipitating aluminum hydroxide by the addition of ammonia, was found to show increased adsorption. A mixture having 23.7 per cent silica, when used as a desulfurising agent, was found to adsorb sixty per cent of the sulfur compounds, while pure silica gel and pure alumina adsorbed 20.0 and 24.8 per cent respectively.

Other adsorbents prepared by these same investigators by suspending finely divided activated carbon in a solution of aluminum sulfate and precipitating the hydroxide by the addition of ammonia showed maximum efficiency with 21.7 per cent carbon in the gel. With this gel, the sulfur removed was 44.8 per cent as compared with 24.7 per cent and 18.2 per cent removal with alumina gel and with activated carbon respectively.

The decoloration properties of silicalized bauxite in kerosene was studied by Chowdhury and Das.[7] Their results with silicalized bauxite show that the greatest removal of

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[6] J. K. Chowdhury and R. C. Bogchi, J. Indian Chem. Soc., 5, 111 (1928).

[7] J. K. Chowdhury and S. C. Das, J. Indian Chem. Soc., 7, 379 (1930).

color was obtained with an adsorbent having about 22 per cent silica. However, a smaller peak was obtained with adsorbents having about 75 per cent silica. With the alumina-silica adsorbents, they obtained maximum removal of color with adsorbents having about 85 per cent silica.

In an attempt to find industrial adsorbents suitable for the adsorption of benzene, Chowdhury and Pal[8] prepared binary mixtures using alumina with silica gel, ferric oxide, and charcoal. In all cases the mixed adsorbents showed increased activity over either of the individual adsorbents in the mixture. The composition of the adsorbents showing the maximum adsorption were 27, 52 and 10 per cent alumina for the mixtures with silica gel, ferric oxide, and charcoal respectively. On mixing bauxite with silica gel, they found that some of the ternary mixtures were not only more active than the individual adsorbents, but were even more active than the optimum binary mixtures.

Since silica gel and charcoal have separately received such thorough investigations, it is only natural that mixtures of these should also be studied. In 1925, Berl[9] observed increased adsorption on silicalised carbon. While investigating the effect of uniformly distributed carbon on

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[8]J. K. Chowdhury and H. N. Pal, J. Indian Chem. Soc., 7, 451 (1930).

[9]E. Berl, Zeit. Ang. Chem., 39, 428 (1925) as cited in J. K. Chowdhury and R. C. Bogchi, J. Indian Chem. Soc., 5, 122 (1928).

the sorptive capacity of silica gel, Fells and Firth[10] were successful in preparing a "carbo-gel" having sorptive power for benzene and toluene superior to either silica gel or active carbon. Their gels were prepared by dissolving cane sugar in 3N hydrochloric acid, then forming a gel by mixing this with sodium silicate of density 1.181. After the gel had set, it was broken into pieces and dried in a steam oven. Following this initial drying and carbonization, the sample was further carbonized in an air oven at 300°C for two hours, then washed with water until free of chlorine. The samples were then dried in a steam oven and finally activated at 600°C for two hours under a pressure of 15-20 mm. The adsorption capacity for benzene and toluene was determined by a dynamic method in which air saturated with the vapor being adsorbed was passed over the adsorbent. It was found that gels having about eighteen per cent carbon were the most active. A summary of their results is given in Table 6.

Shilov, Dubinin and Toropov[11] prepared a series of carbo-silica samples by soaking birch shavings in sodium silicate solutions of various strengths, then carbonizing the shavings by heating them in the presence of zinc chloride.

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[10] H. H. Fells and J. B. Firth, J. Soc. Chem. Ind., 41 39T (1927).

[11] N. Shilov, M. Dubinin, and S. Toropov, Kolloid Z., 49, 120 (1929).

After the zinc chloride had been removed with hydrochloric acid, the gel was washed with water until no trace of the chloride ion was obtained. The adsorbents were then dried at 110°C and activated at 600°C for two hours under vacuum. The adsorption of ammonia, benzene, chlorine, and water vapor on these intimate mixtures was studied. The dynamic method was used for the determination of the sorption capacity for ammonia and chlorine, while with benzene and water a static method was used where the adsorbents were kept in a desiccator containing the liquid being studied until their weights became constant. These investigators found that maximum adsorption was obtained with adsorbents having between sixty and seventy per cent carbon. Their results are summarized in Table 7.

Further experiments with mixtures of carbon and silica gel were carried out by Palkin and Kolesnikov[12] who prepared their adsorbents by adding some activated carbon to dilute waterglass solution and coagulated this by adding hydrochloric acid. The gel that formed was allowed to mature for two to three days in a disiccator, then was dried at room temperature, washed, dried again, and then activated. It was found that samples having ten percent carbon were the most active.

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[12]A. P. Palkin, and A. L. Kolesnikov, Zhurnal Priklaonoi Khimii, 10, 1879 (1934) in Chemical Abstracts, 32 2298-2 (1933).

CHAPTER III

MATERIALS AND EQUIPMENT USED

Materials Used

Sodium silicate.— The sodium silicate solution used in the preparation of the adsorbents was obtained from E. H. Sargent and Company. It was not stable, and the precipitated silica had to be removed before the solution could be used. This was accomplished by diluting the sodium silicate slightly, heating to boiling, and filtering it by means of suction. The resulting clear solution had a specific gravity of 1.2. Solutions of the desired specific gravities were prepared by diluting this solution with distilled water.

Cane sugar.— The cane sugar used was Domino Pure Cane Sugar distributed by the American Sugar Refining Company.

Birch wood.— The birch wood was in the form of a piece of timber one inch by three inches from which shavings were removed as needed.

Zinc chloride.— The zinc chloride was C.P. grade obtained from the J. T. Baker Chemical Company.

Hydrochloric acid.— The hydrochloric acid was C.P. grade.

Benzene.— The benzene was thiophene-free, C.P. grade.

Apparatus Used

Ovens used for drying, carbonization, and activation of Adsorbents.—The oven used for drying the adsorbents was a Thelco Electric Oven with constant temperature regulator, manufactured by the Thermoelectric Instrument Company of Newark, New Jersey. The temperature, measured with a thermometer placed through a hole in the top of the oven, remained at 110±10°C except where noted.

The oven used for the carbonization of the samples is shown in Figure 1. The temperature, measured with a calibrated chromel-alumel thermocouple, was regulated with a powerstat, and was held at 300±10°C except where noted.

Activation of the adsorbents was carried out in an oven similar to the one described above, but the temperature was held at 600±20°C except where noted.

The modified Soxhlet extraction apparatus used for washing the adsorbents.—Of several methods tried for washing the adsorbents, the modified Soxhlet extraction apparatus shown in Figure 3 was selected as being the most satisfactory. With this assembly, as much as 200 ml of adsorbent could be washed at one time with a continuous supply of hot distilled water.

Apparatus for activation of the adsorbents.—To minimize exposure to the atmosphere after activation, the adsorbents were activated in the special 70-ml Pyrex test tubes shown

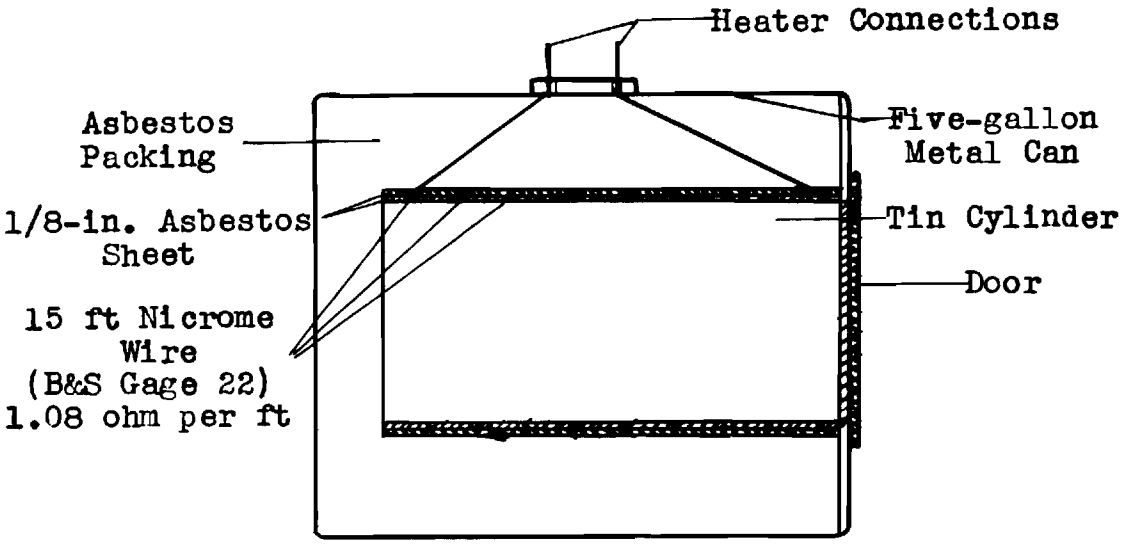

Figure 1

Carbonization Oven

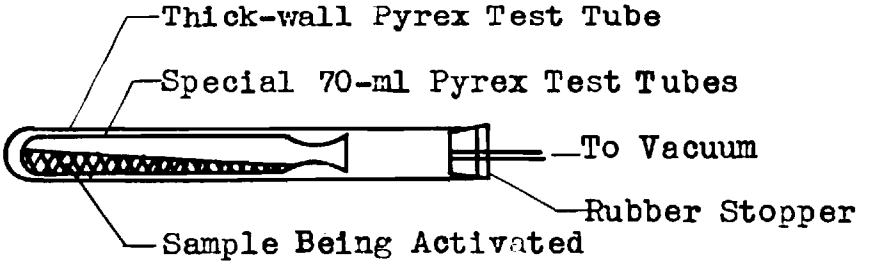

Figure 2

Apparatus for Activation of Adsorbents

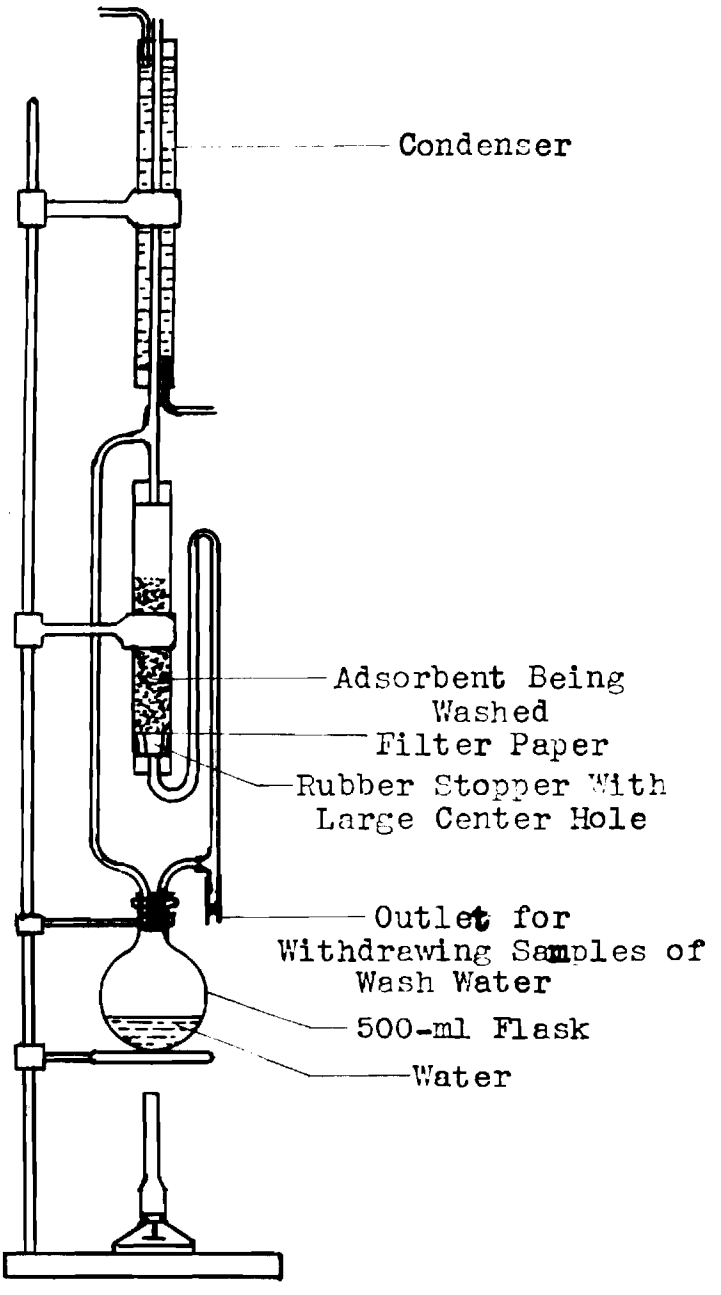

Figure 3

Modified Soxhlet Extraction Apparatus

in Figure 2. These test tubes had the necks narrowed to about one-half inch in diameter to facilitate sealing.

Source of vacuum.—A water aspirator was used as the source of vacuum. The pressure was measured with a mercury manometer to a precision of ± 1 mm.

Apparatus used for the analysis of the adsorbents.—The apparatus used for analysis of the adsorbents was, with minor modifications, identical to that described by Mellor, and is shown in Figure 4.[1] Two five-gallon glass bottles, A and B, were used for storing and delivering the oxygen used for combustion of the carbon in the adsorbents. Bottle A, filled with water used to displace the oxygen in Bottle B, was fitted with a two-hole rubber stopper having a siphon reaching from the bottom of A to the bottom of B. The remaining hole in the stopper was left open to the atmosphere. Bottle B also had a two-hole rubber stopper of which one hole was used for the siphon previously mentioned. The other hole was connected to one side of a three-way stopcock, C, the common side of which led to two 50-ml gas washing bottles, D. The other side of the stopcock was connected to a source of compressed air so that either oxygen or air could be passed through the analysis train as desired.

The two 50-ml gas washing bottles were each filled

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[1]J. W. Mellor and H. V. Thompson, A Treatise on Quantitative Inorganic Analysis. 2d ed. (London: Charles Griffin and Company, Ltd., 1938) pp.631-633.

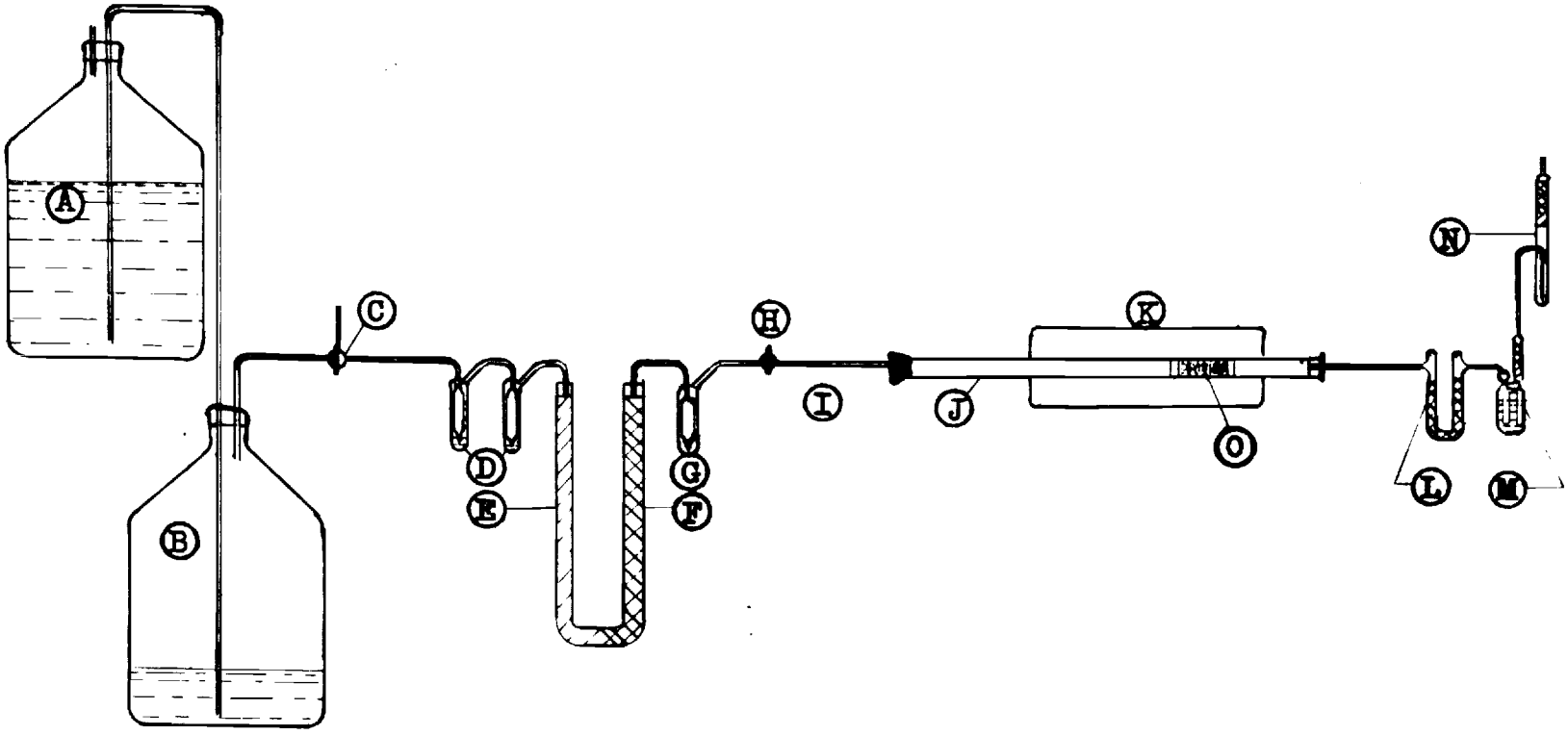

FIGURE 4. APPARATUS USED FOR ANALYSIS OF ADSORBENTS

about one-third full with a ten per cent potassium hydroxide solution to remove any carbon dioxide that might have been present in the oxygen (or air). A large U-tube fifteen inches high constructed of 1¼-inch Pyrex tubing followed. Limb E of this U-tube was filled with granular (8-16 mesh) soda lime to remove any carbon dioxide that might possibly have been left in the gas stream. The other limb, F, of the U-tube was filled with granular (8 mesh) calcium chloride to remove water vapor present in the incoming oxygen (or air). Plugs of glass wool were placed at about three inch intervals in the U-tube to prevent the soda lime and the calcium chloride from being packed too tightly.

Following the U-tube was a final 50-ml gas washing bottle, G, containing about ten millileters of concentrated sulfuric acid which served both as an additional drying agent and as an indicator for the flow rate of the oxygen (or air) passing into the combustion tube, J. The flow rate into the combustion tube was controlled with the stopcock, H.

As a final precaution to remove any water vapor left in the gas stream, a six-inch length of glass tubing, I, filled with indicator silica gel followed and was connected immediately to the combustion tube with a one-hole rubber stopper.

The combustion tube was constructed of 24 inches of 1-inch O.D. silica tubing having a wall thickness of about one eighth inch. The exit end of the combustion tube was

sealed with a one-hole rubber stopper fitted with a six-inch length of glass tubing to which U-tube, L, was connected. This U-tube, constructed from a ten-inch length of ½-inch Pyrex tubing, was filled with calcium chloride to adsorb water eliminated during the analysis. It weighed about 45 gm when charged. To eliminate the possibility of leakage and to minimize the possibility of picking up grease and dirt, the tops were sealed after the tube had been filled with calcium chloride. The calcium chloride (8 mesh) had been saturated with dry carbon dioxide to react with any calcium oxide that might have been present.[2]

Connected to this U-tube was a potash bulb, M, containing 40-50 ml of twenty per cent potassium hydroxide solution. This potash bulb was constructed from 2½ inches of 1½-inch Pyrex tubing. Three bubblers were sealed inside this tube. To prevent the escape of carbon dioxide or water vapor from the bulb, a three-inch length of ½-inch Pyrex tubing which had about two thirds of its length filled with calcium chloride and the remaining one third filled with soda lime, was attached. The weight of this bulb when completely charged was about 120 grams.

Following M was another potash bulb, N, to insure that no carbon dioxide was lost. It was constructed from a

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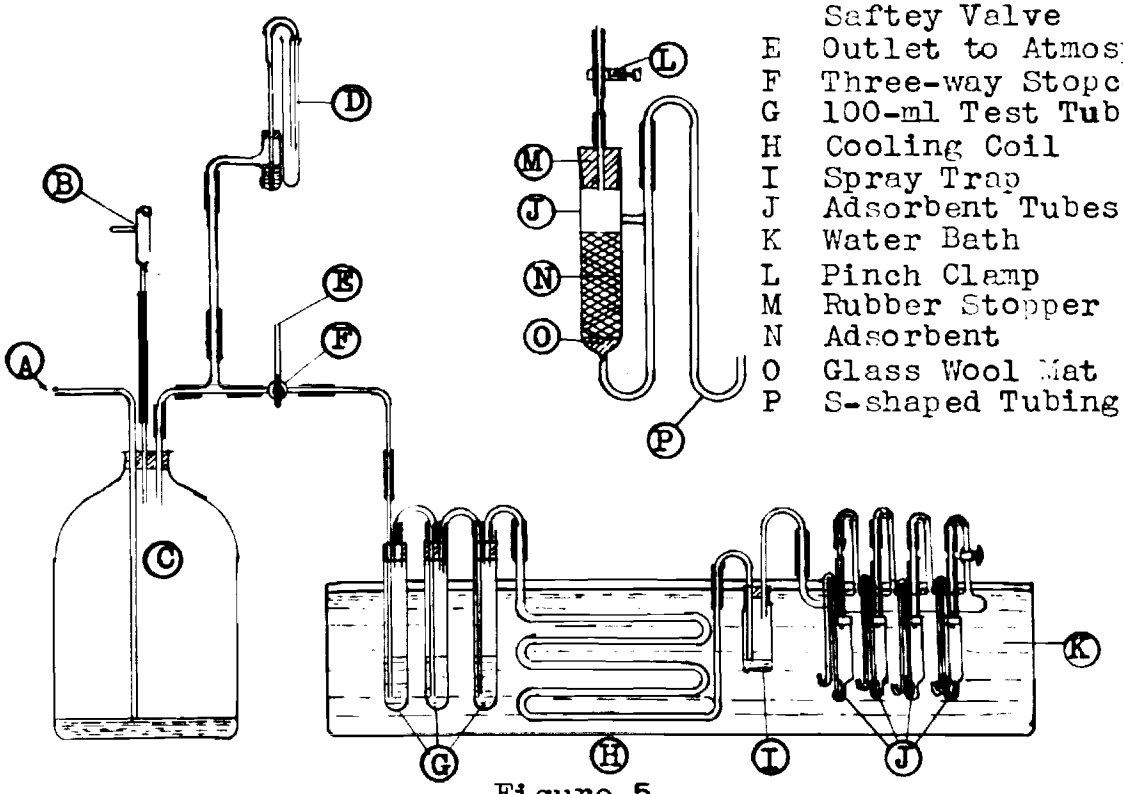
[2]W. C. Pierce, and E. L. Haenisch, Quantitative Analysis. 2d ed. (New York: John Wiley and Sons, Inc., 1940) p. 369.

seven-inch length of ½-inch Pyrex tubing divided into two sections. The lower section was charged with twenty per cent potassium hydroxide solution and the upper section was charged first with soda lime then with calcium chloride.

The electrically heated furnace, K, was used for heating the sample being analyzed. It was thirteen inches long, 5½ inches in diameter, andhad an inner bore of 1¼ inches. The temperature was regulated by a variable resistance. The setting for a temperature of 1000°C was determined before the analyses were begun, and this setting was used thereafter without attempting to measure the temperature.

To insure complete oxidation of the carbon, three to four inches of the exit end of the combustion tube were filled with wire-form copper oxide, O, held in place with plugs of asbestos paper.

Apparatus for the determination of the dynamic adsorption capacity.—The apparatus used for the determination of the dynamic adsorption capacity of the adsorbents is shown in Figure 5. Three 100-ml test tubes A, B, and C were used to saturate the air stream with water vapor. These tubes were each filled about one third full of distilled water. The last two were packed loosely with glass wool to increase the area of contact. A cooling coil, D, constructed of seven feet of 6-mm glass tubing, connected the last of these saturaters to a 200-ml bottle, E, which was filled with glass wool to remove any spray that might be left in the air



A Outlet to Sink
B Aspirator
C Air Reservoir
D Manometer and Saftey Valve
E Outlet to Atmosphere
F Three-way Stopcock
G 100-ml Test Tubes
H Cooling Coil
I Spray Trap
J Adsorbent Tubes
K Water Bath
L Pinch Clamp
M Rubber Stopper
N Adsorbent
O Glass Wool Mat
P S-shaped Tubing

Figure 5

Apparatus for the Determination of the Dynamic Adsorption Capacity

stream. Following this spray trap was a nine-inch length of 1-inch Pyrex tubing, F, to which were sealed four pieces of $\frac{1}{2}$-inch Pyrex tubing for attaching the adsorbent tubes to the train.

The adsorbent tubes (see Figure 5) were constructed from four inch sections of 7/8-inch Pyrex tubings. A mat of glass wool was placed in the lower end of each of the adsorbent tubes to prevent the outlet from becoming clogged by the sample. After the sample had been introduced, the adsorbent tube was stoppered until the sample could be used.

The adsorbent tubes were attached to the train in such a manner that the air stream flowed downward through the adsorbent, preventing any lifting of the sample. An S-shaped section of glass tubing was attached to the exit end of this tube to prevent any water from the water bath getting into the tube. The upper bend of this tubing was about one inch above the surface of the water and the lower bend was below the surface of the water so that the flow rate could be observed. Screw clamps, placed between the adsorbent tube and the point of attachment to the train, were used to regulate the flow of the air through the adsorbents. To enable more precise control of the flow rate during the determination of the break point, a stopcock was used in place of the screw clamp.

A break point indicator similar to that described

by Anderson[3] is shown in Figure 6. It consisted of a bit of calcium chloride 2-mm in diameter and 10-mm in length which was fused across the ends of two copper wires. This was enclosed in a small glass T-tube constructed from a 10/30 ground-glass joint. To the other ends of the copper wires was attached a Model RC 16 conductivity bridge manufactured by Industrial Instruments, Inc., Jersey City, N.J. This was used to measure the resistance of the calcium chloride. With this instrument it was possible to measure resistances from 0.02 to 2,500,000 ohms with a precision of 0.5 to 1 per cent.

The rate of flow was controlled by a capillary type flow meter which immediately followed this break point indicator.

The entire adsorbent train, with the exception of the break point indicator and the flowmeter, was submerged in a fifteen gallon water bath thermostated at 25±1°C by means of an electric heater operated by an electronic relay circuit patterned after that described by Redfern.[4]

Compressed air system.—The compressed air used for the air stream was obtained from two separate sources. A rotary oil vacuum-pressure pump manufactured by G. F. Nelson of Berkeley, California, was used in the majority of the runs.

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[3] P. Anderson, J. Chem. Soc., 121, 1155 (1922).

[4] S. Redfern, Ind. and Eng. Chem. Anal. Ed., 14, 64 (1942).

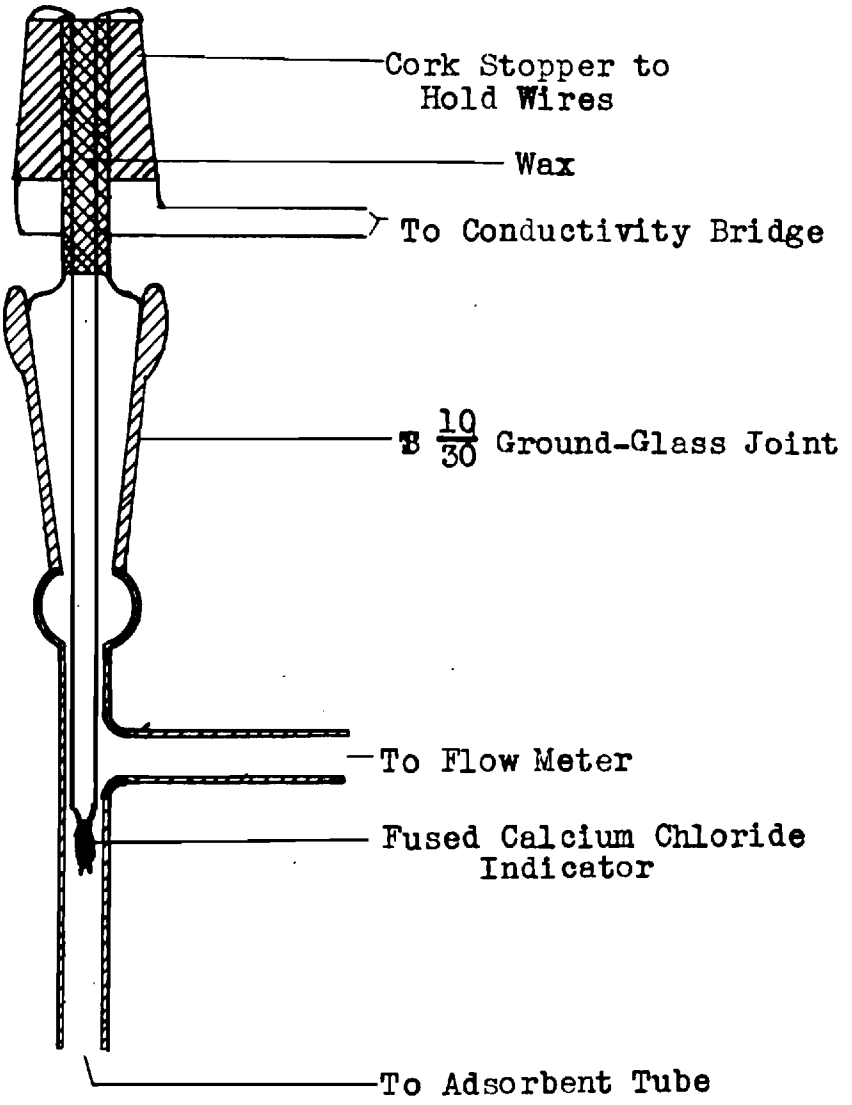

Figure 6

Break Point Indicator

However, this pump emitted oil vapors. Removal of these vapors was accomplished by placing plugs of cotton in the air line. During a portion of the time the oil pump was broken and compressed air was obtained with a water aspirator connected as shown in Figure 5. Although the oil pump seemed to give a more uniform pressure, it presented the added difficulty of having to remove oil vapor from the air stream.

A five-gallon bottle was used as an air reservoir for both systems. A small mercury manometer was attached to this reservoir and served as both a pressure indicator and as a safety valve.

Apparatus for the determination of the static adsorption capacity.—The apparatus for the determination of the static adsorption capacity consisted simply of a supply of ground-glass-stoppered weighing bottles and a desiccator which contained the adsorbate being studied.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Preparation of the Adsorbents

Intimate Mixtures of Silica and Carbon from Cane Sugar[1]

Mixing.— The adsorbents composed of intimate mixtures of silica and carbon obtained from cane sugar were prepared according to the method of Fells and Firth.[2] The cane sugar was first dissolved in hydrochloric acid of specific gravity 1.051 (about 3N). Sodium silicate of specific gravity 1.183 was then added slowly to this solution with stirring. Equal volumes of hydrochloric acid and sodium silicate were used in all cases. Adsorbents of varying carbon content were prepared by altering the amount of sugar dissolved in the hydrochloric acid. To obtain adsorbents having high carbon content, sugar was dissolved in distilled water, the acid added to the resulting solution,

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[1]See Table 1-A for details of preparation of specific samples.

[2]H. H. Fells and J. B. Firth, J. Soc. Chem. Ind., 41, 39T (1927).

and sodium silicate then added.

It was found during preliminary investigations that gels of more uniform appearance were formed when the sodium silicate was added to the acid-sugar solution than when the acid-sugar solution was added to the sodium silicate. It was also observed that the temperature of mixing affected the appearance of the gels. If the solutions were mixed at room temperature or higher (30 to 60°C) a white flocculent precipitate formed in nearly every case. Slower addition of the sodium silicate and more thorough mixing seemed to decrease the amount of this precipitate formed, but did not eliminate it. However, when the solutions were cooled to 0 to 10°C before mixing, the precipitate was either materially decreased or eliminated completely. Since mixing at low temperature resulted in the formation of gels having a uniform appearance throughout, this procedure was used after its effect was recognized.

The resulting hydrochloric acid-sugar-sodium silicate solutions were perfectly clear except for the cloudiness due to the presence of the flocculent precipitate. Usually within 8 hours the solutions had set to firm gels, but they were allowed to stand for about 24 hours from the time of mixing before they received further treatment. Samples having high sugar content did not gel.

After the 24 hour standing period, the gels were very firm and gave a vibrating, musical sound when the beakers

containing them were struck. In some cases the gels had contracted, causing the material to pull away from the beaker, and causing cracks to form throughout the interior of the gel. When this occured, several milliliters of acidic liquid were present on the surface.

Initial drying.— The gels were then cut into pieces ranging up to 3/4 inch in diameter and dried at 75 to 126°C for 2 to 46 hours. The solutions of samples of high carbon content which did not gel were dried out under the above conditions. During this drying the gels turned dark brown or black due to the decomposition of the sugar. On their surfaces there formed long, white, matted crystals of sodium chloride.[3]

The samples having very high carbon content frothed and spilled over the sides of their containers during this drying. To prevent this material from getting on the oven, beakers containing these samples were placed in large pans to catch the overflow.

Carbonization.— Following this drying the samples were further carbonized in covered beakers at 290 to 375°C for 1.7 to 4 hours. They were then removed from the oven, covered with watch glasses, and left standing until they could be washed.

Washing.— Several methods for washing the samples were used,

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[3]The formation of these crystals has been reported by H. H. Fells and J. B. Firth, Proc. Roy. Soc., 1926, A112, 468. Photographs are also given.

but the modified Soxhlet extraction apparatus was used in all cases except with samples 1-8. These were washed with a continuous flow of hot distilled water while on a funnel. In all cases the washing was continued until no test for the chloride ion was obtained when a drop of silver nitrate was added to a few milliliters of the wash water. The time for the complete removal of the chloride ion varied from several hours for samples having high silica content to several days for samples having high carbon content.

During the washing, discoloration of the wash water was observed with some of the samples. This discoloration, assumed to be due to decomposition products formed during the carbonization of the sugar, was very difficult to remove by washing with water. Samples 9 and 10 were washed with methyl alcohol using the Soxhlet extraction apparatus. This resulted in the almost complete removal of the products causing discoloration.

Drying.— The washed adsorbents were then dried at 98 to 120°C for 2 to 26 hours, then placed in stoppered test tubes until they could be activated.

Activation.— Activation was accomplished by heating 5 to 20 grams of each adsorbent at 500 to 640°C for 2 to 3 hours under a vacuum of 18 to 247 mm of mercury obtained with a water aspirator. The above figures represent the extreme values. The conditions desired were activation at 600°C for 2 hours under a vacuum of 15 to 20 mm. Conditions for the

individual adsorbents are given in Table 2.

After the activation, the samples were sealed in their containers and kept until they could be used. To facilitate the opening of the sealed tubes, a neck between one and two inches was left when the tubes were sealed. When time was available, each container was opened and samples were removed for the analysis, for the determination of the static adsorption capacity with water and benzene, and for the determination of the break point and dynamic adsorption capacity with water. The remainder of each sample was immediately resealed in the same container.

Another series of activations was carried out at 300°C on another portion of the sample in the same manner as described above.

Intimate Mixtures of Silica and Carbon from Birch Wood[4]

Mixing and carbonization.— The adsorbents composed of intimate mixtures of silica and carbon from birch wood were prepared according to the method described by Shilov, Dubinin, and Toropov,[5] and Honig.[6] Shavings of birch wood were soaked in sodium silicate solutions of varying concentrations for

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[4]See Table 1-B for details of the preparation of specific samples.

[5]N. Shilov, M. Dubinin, and S. Toropov, Kolloid Z., 49, 120 (1929).

[6]Von P. Honig, Kolloidchem Beih., 22, 353 (1926).

a period of a week or longer, then the excess sodium silicate was pressed out under suction. The soaked shavings were then transferred to a beaker, zinc chloride solution (specific gravity 1.935) added, and the mixture heated over a bunsen burner. At about 110°C the zinc chloride solution began to boil and the shavings began to darken. Between 120 and 150°C the shavings dissolved completely, giving dark, fairly viscous solutions which began thickening at about 155°C. By the time the temperature had reached 175°C the solutions were very thick and tarry. Heating was continued until the solutions became too thick to stir or else began smoking (168 to 290°C), then they were allowed to cool. On cooling they solidified, forming black tarry residues which had to be heated slightly before they could be removed from the beakers. These residues were transferred to 150 ml test tubes and heated slowly under vacuum in an electric oven for 6 to 7 hours to a final temperature of 300°C. The samples were then removed from the oven and cooled.

Washing.— The hard, coke-like material was crushed in a mortar and washed with 4N hydrochloric acid until a test showed that no zinc ion was present. To test for the presence of zinc, 2 to 20 ml of the acid filtrate were evaporated to dryness in a 100-ml test tube and the residue dissolved in approximately two milliliters of distilled water. To this was added several drops of sodium sulfide solution. When no precipitate or cloudiness due to the formation of

zinc sulfide was observed, washing was assumed to be complete for the removal of the zinc.

Each sample was then transferred to the Soxhlet and washed free of chloride ion as described previously.

Drying and activation.[7]—The drying and activation of the samples was carried out at 600°C as previously described.

Analysis of the Adsorbents

Samples used for the analysis were poured into ground-glass stoppered weighing bottles and kept in a desiccator over phosphorous pentoxide until the analyses had been completed. The analyses were usually begun within a half hour after the samples had been removed from their sealed tubes. In most cases two analyses were run. During the period between the first analysis and the second analysis, the adsorbent showed a definite gain in weight even while kept over phosphorous pentoxide. No correction was made for this observed increase in weight since the cause was unknown.

Before a series of analyses was begun, the combustion tube was thoroughly dried by heating it to approximately 1000°C for about one hour while a stream of dried oxygen was passed slowly through it. The tube was then allowed to cool while the flow of oxygen was continued. During this

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[7]See Table 2 for individual activation conditions.

cooling the calcium chloride and the potash bulbs were weighed and made ready for the analysis.

The 0.1 to 0.5 grams of sample used for each analysis was poured directly from the weighing bottle into the clay boat and was placed immediately in the combustion tube. The calcium chloride tube and the potash bulbs were attached, and combustion in the stream of oxygen was started. The rate of flow of the oxygen was such that only one to two bubbles per second passed through the sulfuric acid bubbler. The weighing bottle was then weighed and replaced in the desiccator.

Heating was such that a temperature of 900 to 1000°C was reached in about 45 minutes. Heating at this temperature was maintained for an additional one to two hours, then was discontinued. The calcium chloride tube and the potash bulbs were disconnected, their end sealed with short lengths of rubber tubing and their surfaces wiped with a damp cloth to remove any grease or dirt. They were allowed to dry for fifteen minutes then weighed. Tares were used in each of the above weighings.

The clay boat, with its contents, was moved to a cool portion of the combustion tube and was allowed to cool in a slow stream of oxygen, then weighed. The residue in the boat was then placed in a stoppered vial, labeled, and stored.

From the gain in weight of the calcium chloride tube, the weight of water was found. This water was due to water adsorbed by the adsorbent and the water formed by the combustion of any hydrogen in the adsorbent. Correction for this was made by the method outlined in the appendix.

From the gain in weight of the potash bulbs, the amount of carbon dioxide formed was found. The amount of carbon was calculated by multiplying the weight of carbon dioxide by 0.273, the gravimetric factor for the determination of carbon in carbon dioxide.

The amount of silica was determined from the difference in weight of the boat with the residue and the empty boat. The residue was assumed to be pure silicon dioxide.

Determination of the Adsorption Capacity

Dynamic Method

Break point determination.— The break point is defined as the time at which the first bit of adsorbate is found in the effluent air stream. For water vapor, the only adsorbate used in this investigation for the dynamic determinations, the break point was very conveniently determined with the break point indicator described previously in Chapter III.

At the beginning of each break point determination, the indicator was attached to the adsorbent tube. Air

saturated with water vapor was then passed through the adsorbent, then through the break point indicator and flowmeter to the atmosphere. As soon as the adsorbent failed to completely remove all of the water vapor from the air stream, part was adsorbed on the fused calcium chloride, causing the resistance of the calcium chloride to decrease. This change in resistance was measured with the conductivity bridge. A plot was made of conductivity bridge reading as a function of the time taken, and from this the time of the break point was calculated (see the Appendix). The flow rate was held at 100±50 ml per minute. When sufficient readings were obtained with the conductivity bridge to plot a smooth curve, the adsorbent tube was removed from the adsorbent train, dried, and weighed.

Before each break point determination it was necessary to check all connections to make sure that they were perfectly dry and that no moist air was in any of the tubing. The indicator was so sensitive that moisture in the air in the tubing was frequently enough to cause the resistance to decrease to a value such that the indicator was useless. A measure of the sensitivity is given in the Appendix. In order to obtain a sharp indication of a break point it was necessary that the resistances be 50,000 ohms or greater. During the beginning stages of the determination it was not unusual for the calcium chlorides to dry out in the air stream and reach a resistance in excess of 2,500,000 ohms.

Saturation of the samples.—After the adsorbent tube had been weighed to determine the amount of water adsorbed at the break point, it was again placed in the dynamic adsorption train and the adsorbent allowed to continue saturating. Every few hours the adsorbent tube was removed from the train, dried and weighed, then replaced. This was continued until no further gain in weight was observed. Saturation by the dynamic method required 50 to 175 hours.

During saturation the flow rate varied between 80 and 300 ml per minute. An approximate check was exercised by bubbling the effluent air through water and observing the rate of formation of the bubbles.

Static Method

The static adsorption capacity was determined in a manner similar to that used by Shilov, Dubinin, and Toropov.[8] From 0.2 to 2 grams of each adsorbent was poured into glass-stoppered weighing bottles, and these were placed open in a closed desiccator containing the adsorbates being used. Every few days the samples were removed from the desiccator, weighed, then replaced. This was continued until no further gain in weight was observed. This process required approximately a month for saturation to be reached.

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[8] Shilov, Dubinin, and Toropov, op.cit., p. 121.

Due to shortage of equipment no attempt was made to thermostat the samples except to minimize the effect of the fluctuation in room temperature by standing the desiccators in tubs of water. The observed temperatures at the time of weighing varied between 17 and 26°C. Final weighings were made at 25.1°C.

When saturation was reached the adsorbents were labeled and stored.

CHAPTER V

DISCUSSION

Discussion of Results of Analyses

Accuracy of the analyses.— In all, 36 adsorbents were analyzed, 31 of these being analyzed in duplicate or triplicate. Lack of time prevented all samples from being checked by running duplicate analyses.

Maximum deviations in the results of duplicate analyses for silica, carbon, and water were as follows: silica, 4.7 per cent; carbon, 12.1 per cent (sample 18-0); and water 21.0 per cent (sample 1D-A). The average of the maximum deviations were 1.0 per cent, 1.9 per cent, and 3.0 per cent for silica, carbon, and water respectively. The second largest maximum deviations for carbon and water respectively were 6.6 and 6.2 per cent. This gave an average maximum deviation, when the extreme maximum deviations mentioned above were omitted, of 1.5 per cent for carbon, and 2.4 per cent for water.

Except for adsorbent 18-0 mentioned above, all analyses of each adsorbent were averaged, and the average result used as a basis for further calculations. For adsorbent 18-0 the analysis giving the highest result was

used, since it was more in keeping with the other results. This was felt to be justified since this adsorbent was one of the first that was analyzed and the technique had not been mastered. The last analysis was the one reported.

This averaging process, while standard procedure in most analytical work, might be open to question in the case of the analyses reported here. It was noticed that if two or more analyses were run on a given adsorbent and the results differed appreciably, the analysis showing the highest percentage of silica usually showed the lowest percentage of carbon and water. It was further noticed that the difference between the two analyses for silica and the two analyses for carbon were about the same. This would indicate that the sample showing high silica had not had all the carbon burned out. Possibly the best single analysis after making the above considerations should have been used.

The conclusions drawn by using the above analyses would be unaffected since making the above correction would cause, at most, an increase of the carbon content of 3.3 per cent.

In Chapter IV it was mentioned that samples standing in the desiccator while waiting for the analyses to be run showed a definite gain in weight. This gain varied from practically zero over a period of about one day for samples having high silica content, to as much as 0.6 per cent

(sample 23-A) over a period of eight days for samples having high carbon content. A second and third analysis on sample 23-A gave essentially the same results as the first. An additional gain in this sample of 0.065 per cent twelve hours after making the second analysis was noticed.

Because the high silica samples showed the least gain, and because the samples were kept in a desiccator over phosphorous pentoxide, it seems certain that the increase in weight was not due to adsorption of water, but was due to the adsorption of oxygen or some other gas present in the air.

Trends observed.— In most of the analyses, the total of the per cent silica, carbon, and water was more than 100 per cent. This indicated an error either in the assumption made of the materials present or in the experimental technique. Since the water content found from the analyses seemed unusually high for substances dried out at 300 to 600°C, it was thought that perhaps the adsorbents took on water during the time of transfer from the weighing bottle to the combustion boat. This possibility was eliminated when the curves (see Figure 18) showing the rate of adsorption of water vapor from saturated air were examined. From these it is seen that the gain in weight due to adsorption of water would be negligible in the 0.5 to 2 minutes required for transferring the sample. The chance of the presence of water vapor in the stream of oxygen used for combustion was

also eliminated by placing a six-inch section of tubing filled with indicator silica gel in the oxygen stream before the gas entered the combustion tube. No indication of any water vapor being present was shown by the gel.

Since the carbon present in the adsorbents was obtained from an organic source (i.e., sugar or birch wood), it was thought that perhaps hydrogen from some organic compound was reacting with the oxygen and forming water. The probability that this is a compound of carbon and hydrogen is small because of the high temperature of activation. Most organic compounds likely to be present as a result of the carbonization of sugar would either distill off or decompose at 600°C. When the analyses were corrected according to the method outlined in the Appendix, some very interesting trends came to light.

It was observed that both the water content and the hydrogen content of the adsorbents increased almost directly with the carbon content. It was also found that more hydrogen was on the adsorbents activated at 600°C than was on those activated at 300°C.

In Figure 7 the per cent water found in the sample after making the above mentioned corrections is shown as a function of the per cent carbon in the sample. From this Figure it is seen that the water content of the adsorbents increases with increase in the carbon content, being roughly directly proportional to the carbon present. This is

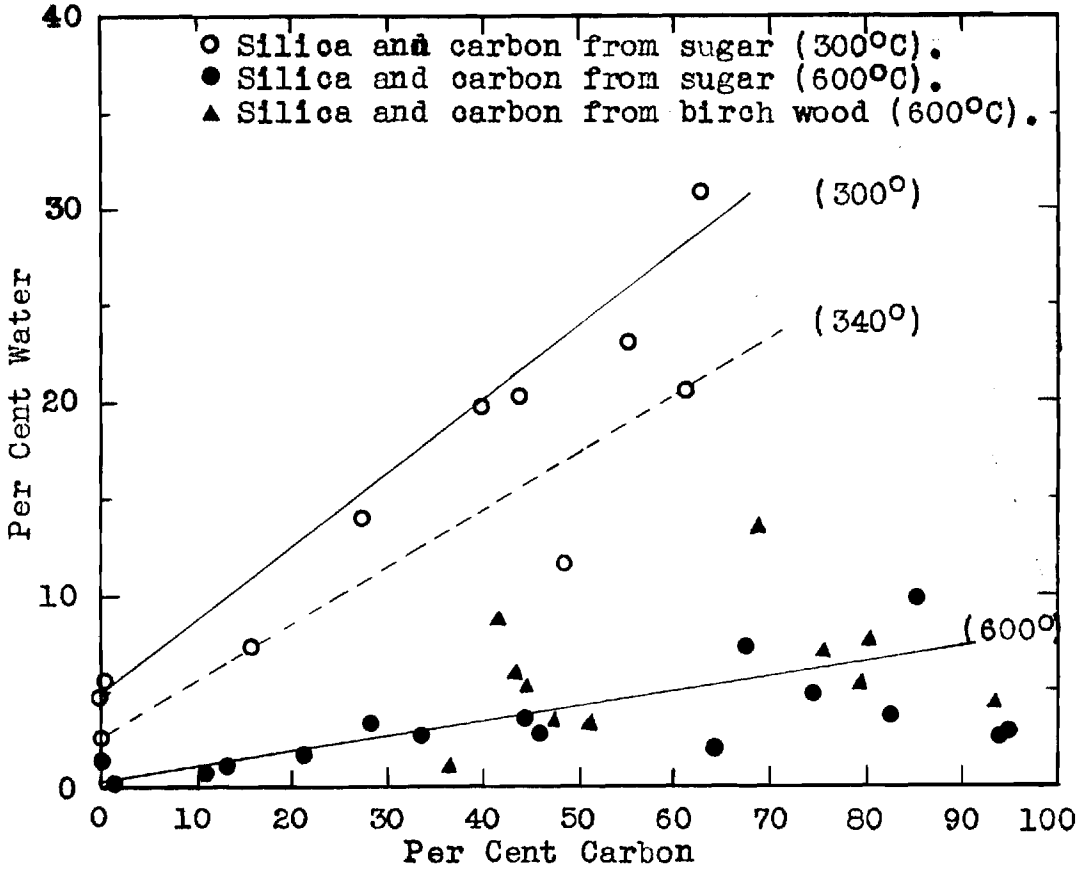

Figure 7

Water Content of the Analyzed Adsorbents

contrary to what one would expect from the affinity of charcoal for water vapor since charcoal is usually less active toward water than is silica.

One sees also from Figure 7 that the amount of water in the adsorbent decreases with increased temperature of activation. This is in line with what one would predict. Samples 5, 10, and 16 were activated at temperatures reaching 340 to 350°C, and the percent water in these samples lies below that of the samples activated at 300°C. The water in sample 12 lies even further below the line than the other points. However, during the carbonization, the temperature of this sample reached 375°C.

The adsorbents having carbon obtained from the two different sources show essentially the same water content when activated at 600°C.

Equally interesting are trends shown when the per cent hydrogen is plotted as a function of the per cent carbon, both having been corrected as mentioned above. Figure 8 shows these results. It is seen that the per cent hydrogen on the adsorbents also increases with the carbon content.

From Figure 8 it is also seen that the hydrogen content increases with increased activation temperature.

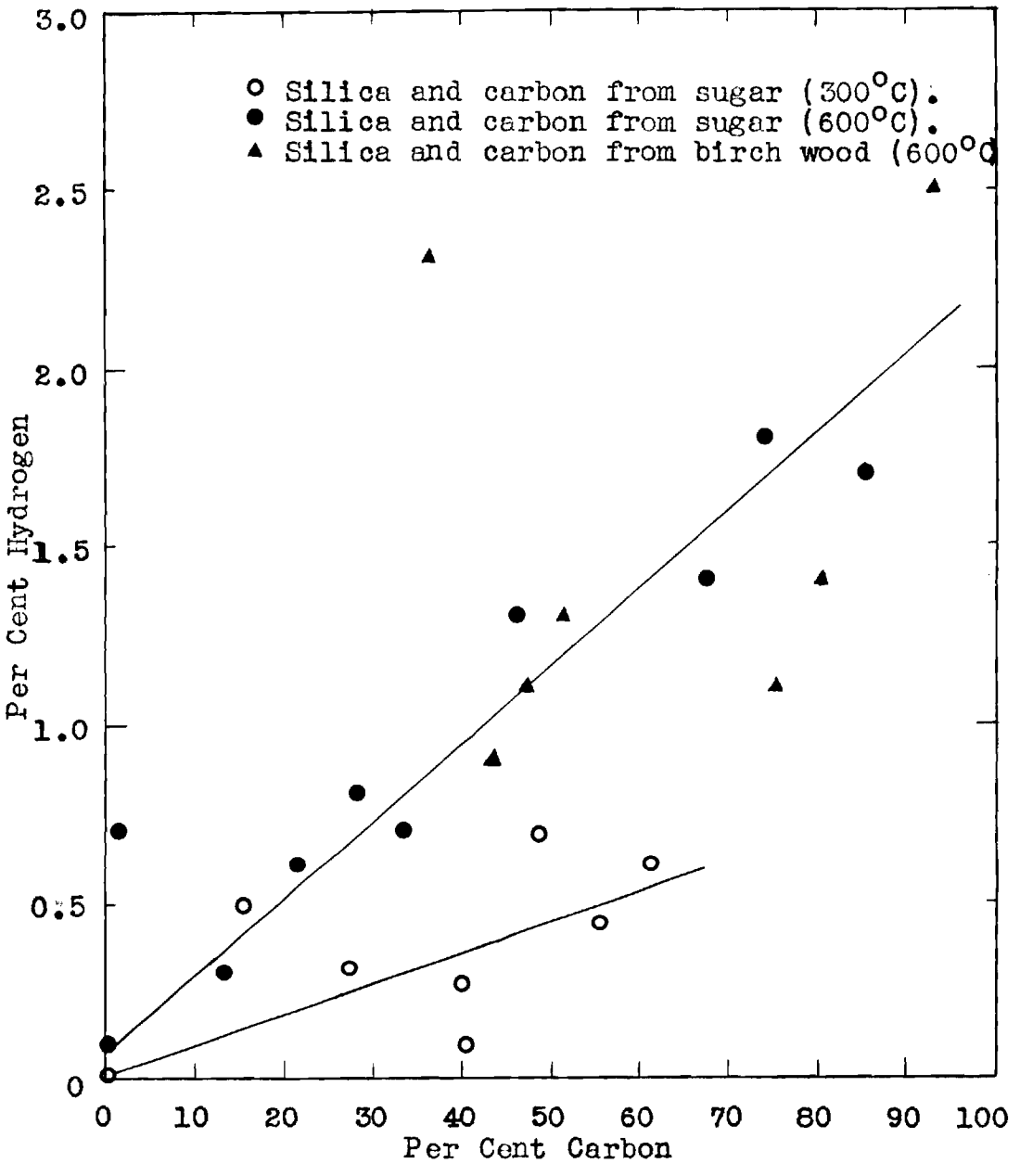

Figure 8

Hydrogen Content of the Mixed Adsorbents

Comparison of the Results Obtained by the Dynamic and the Static Method

The dynamic method gave results which were consistently lower than those obtained by the static method, but only by three per cent or less in most cases. The results are shown in Table 4 and in Figures 9, 10 and 11. For some reason the dynamic method gave results for samples 9-A and 15-A which were eight and six per cent higher respectively than the corresponding static values. The cause of this is not known.

That the dynamic method should give the lower result is easily explained since there is always present in this method the chance of losing some of the smallest adsorbent particles in the air stream. Although an attempt was made to prevent loss from this cause, it is known that it was not entirely successful since small amounts of the samples were found in tubing that followed the adsorbent. Loss of the adsorbent would show up in the results as a decrease in the capacity of the adsorbents.

As would be expected, the dynamic method was the more rapid of the two methods, and required about four to eight days for the samples to reach constant weight. This was about one fourth the time required for the static method.

From the industrial standpoint, the dynamic method is also superior since it involves conditions more nearly

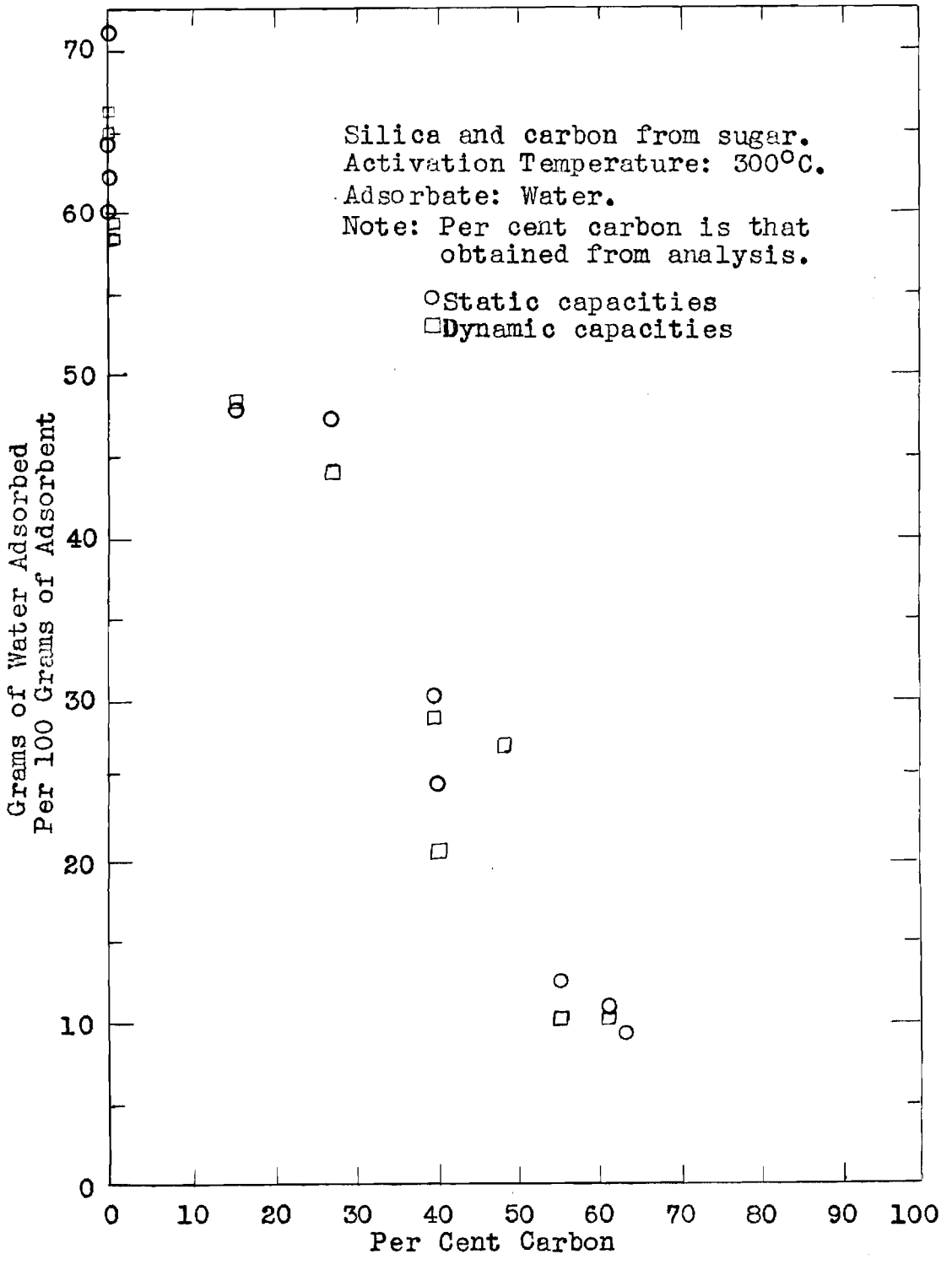

Figure 9

Comparison of the Static and the Dynamic Saturation Capacities

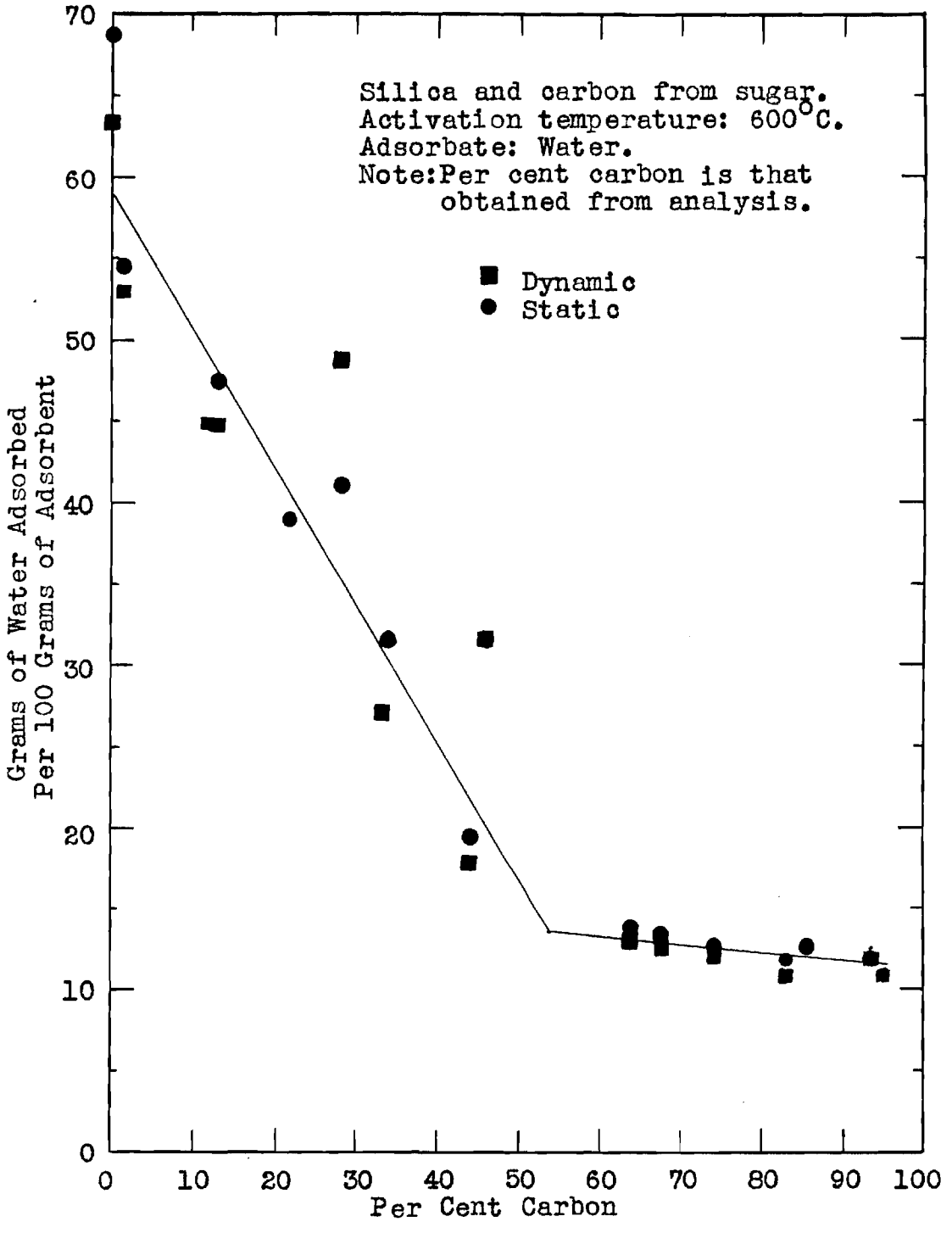

Figure 10

Comparison of Static and Dynamic Saturation Capacities

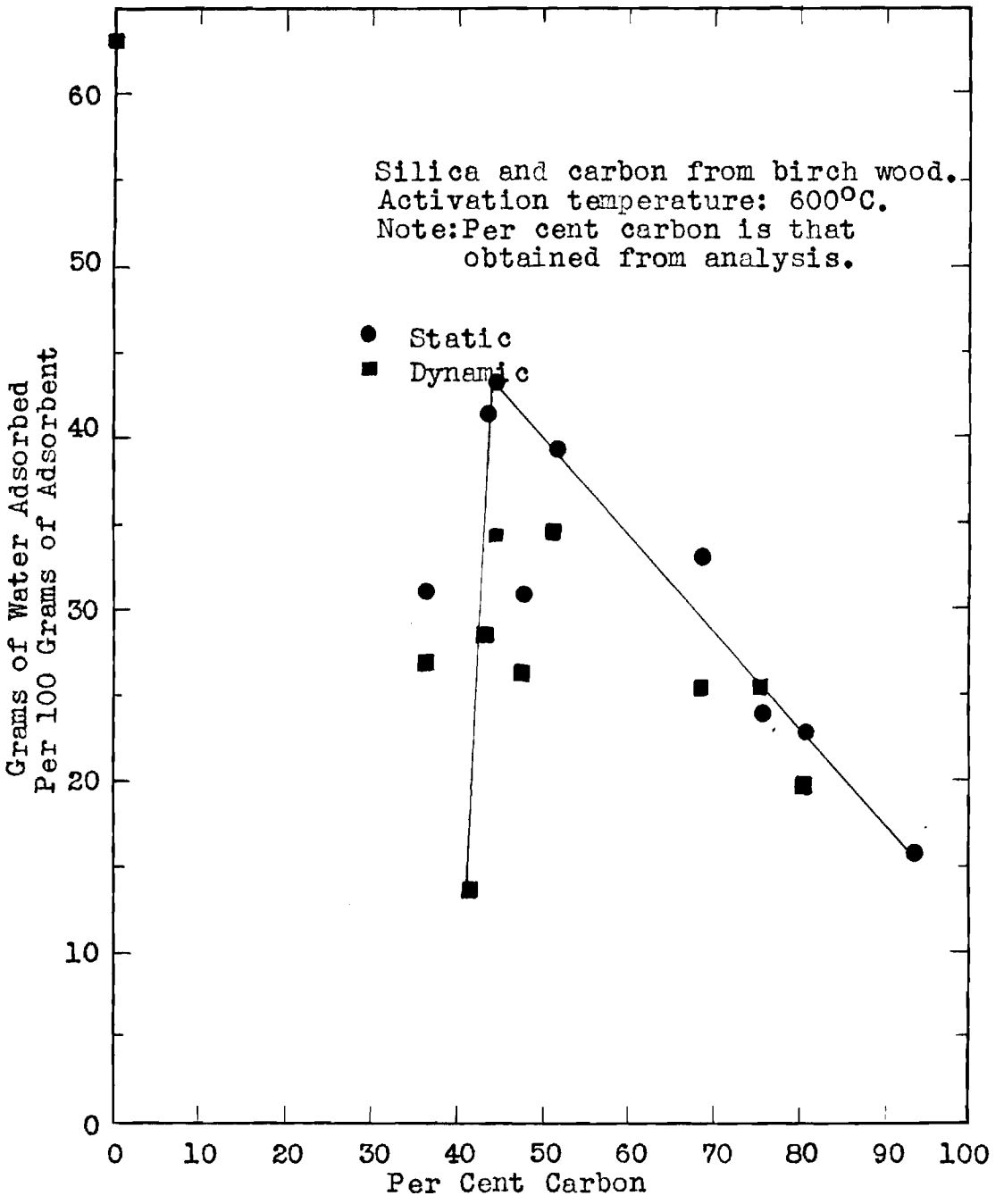

Figure 11

Comparison of Static and Dynamic Saturation Capacities

approaching those found in industry. Also, it is possible to obtain information on break points, which is of industrial importance.

The static method has its advantages if just the saturation value of the adsorbent is desired. Once the sample has been prepared and placed in contact with the vapors of the adsorbate being studied, no further time has to be spent except to make weighings every few days, or weeks, to determine when saturation has been reached. Then too, there is the advantage that there is no chance for loss of any adsorbent.

The Effect of Increasing the Carbon Content of the Adsorbents

Effect on the rate of adsorption.— Increasing the carbon content of the adsorbents was found generally to decrease the rate of adsorption. See Figure 12 where rate of adsorption curves of selected samples are shown. From this Figure it is seen that high silica samples adsorbed water faster than did the samples having high carbon content. Fells and Firth reported that "... it was found that varying the proportions of the carbon did not materially affect the rate of adsorption."[1] This is possibly true for their adsorbents, but, except for their straight charcoal sample,

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[1]H. A. Fells and J. B. Firth, J. Soc. Chem. Ind., 41, 39T (1927).

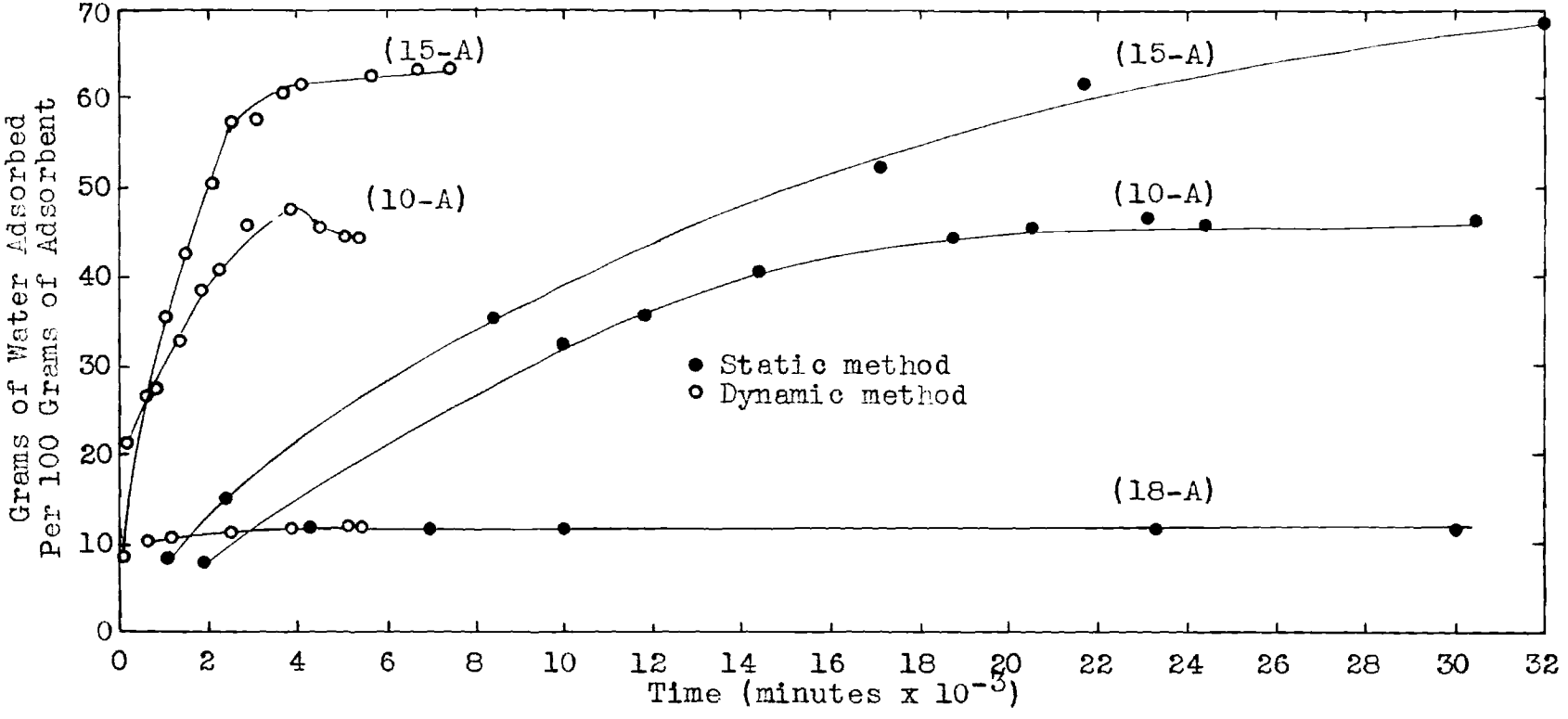

Figure 12

Rates of Adsorption of Water

they reported no investigations of adsorbents in the range 41 to 100 per cent carbon.

After the initial stage of adsorption, during which time the large majority of the total adsorbate was taken up, all samples continued to gain weight at essentially the same rate until saturation was reached. The time for this leveling out process to begin increased with the decrease in carbon content, and required 15 to 80 hours for the dynamic method, and 60 to 530 hours for the static method. In the case of adsorption of benzene, the leveling out process began within 48 hours, and from then until saturation was reached the adsorbents all gained weight at essentially the same rate.[2]

Effect on the break point.—Results of the determination of the break point using water vapor as adsorbate are given in Table 5 and in Figure 13. Figure 13 shows the grams of water adsorbed at the break point per 100 grams of adsorbent plotted as a function of the per cent carbon in the sample. The water ranged from zero for sample 18-0 to 9.7 per cent of the adsorbent weight for sample 10-0.

With both of the series of adsorbents from silica and carbon from cane sugar, and with the adsorbents of silica and carbon from birch wood, the same general trend is

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[2]For a listing of investigators who have studied the rates of adsorption of various vapors by charcoal, see J. W. McBain, The Sorption of Gases by Solids, p. 52.

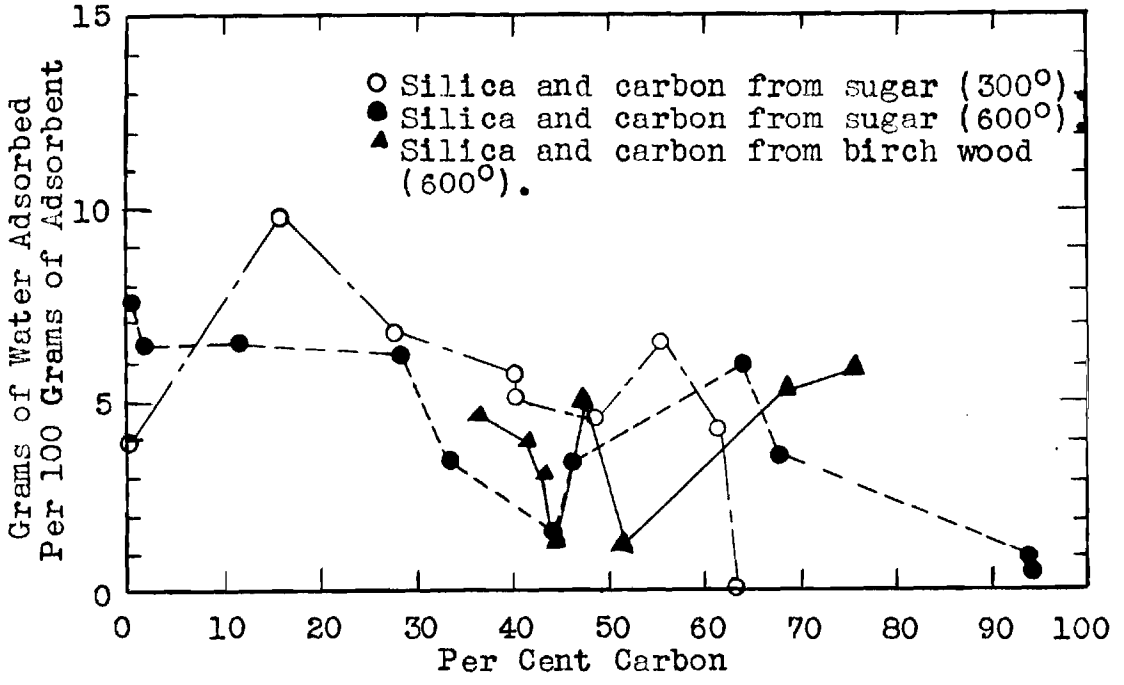

Figure 13

Effect of the Carbon Content
on the Break Point Capacity with Water

observed. From Figure 13 it is seen that a minimum of activity is found in the neighborhood of 40 to 50 per cent carbon. Also it is seen that the activity increases until the carbon content reached 50 to 65 per cent in the cases of the samples prepared using sugar. The samples from birch wood show similar behavior, but no break points in this series were run on adsorbents having greater carbon content than 76 per cent. Also, a maximum is indicated in the neighborhood of 15 per cent carbon for the 300°C activated sugar samples. Since no samples could be prepared from birch wood by the procedure used of lower carbon content than 36 per cent, no comparison can be made in this range.

These observations are interesting because both peaks mentioned above lie in the vicinity of the compositions reported by Fells and Firth, and by Shilov, Dubinin and Toropov for adsorbents showing maximum capacity at saturation.

Another point of interest which might be mentioned is the behavior shown by samples 2D-A, 6D-A, and 12D-A. Both 2D-A and 12D-A show capacities appreciably geater than sample 6D-A when saturation was finally reached, but in the break point determination, sample 6D-A showed an activity of about three times that of the other two adsorbents.

These trends observed in the break point might or might not be significant. In determining the break point, samples varying from 1.3 to 11.1 grams were used with flow rates of 60 to 150 ml per minute. Whether or not the amount

of sample, the flow rate, the particle size, the time of contact of the air stream with the adsorbent, and other variables exert appreciable influence on the break point or not was not determined.[3]

The fact that the same general trend for all three series of adsorbents, and in particular the two series in which the carbon was obtained from two entirely different sources (i.e., sugar and birch wood) would indicate that the results are not entirely due to chance.

Effect on the saturation value.—The effects of the carbon content on the capacities for water of the adsorbents at saturation are shown in Figures 9, 10 and 11, and for benzene in Figures 14 and 15. These Figures show the amount of adsorbate per 100 grams of sample as a function of the per cent carbon as it was found from the analyses. For comparison purposes, results obtained using benzene as adsorbate are shown together with the results reported by Fells and Firth, and by Shilov, Dubinin, and Toropov with the same adsorbate in Figure 16.

The results obtained in the work herein described duplicate the work of neither of the above mentioned groups.

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[3]For a report of factors affecting the rates of water adsorption from air by silica gel, see J. E. Ahlberg, Ind. Eng. Chem., 31, 988 (1939); W. L. Ross and E. R. McLaughlin, Refrig. Eng., 59, 167-73 (1951); and P. Demougin, Mem. Poudres, 25, 18-90 (1922-33) as cited in Chemical Abstracts, 27, 1559.

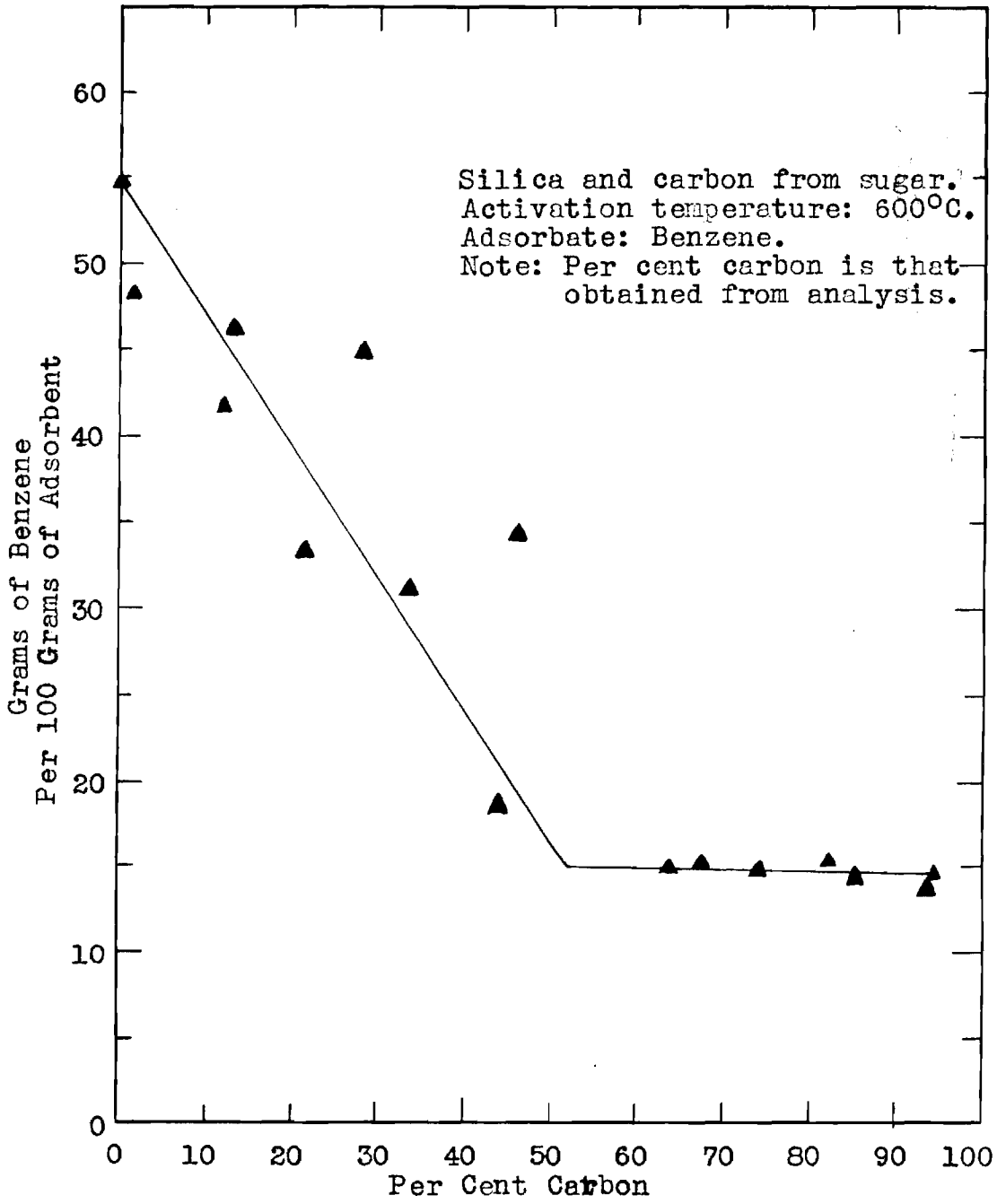

Figure 14

Effect of Carbon Content
on the Saturation Capacity for Benzene

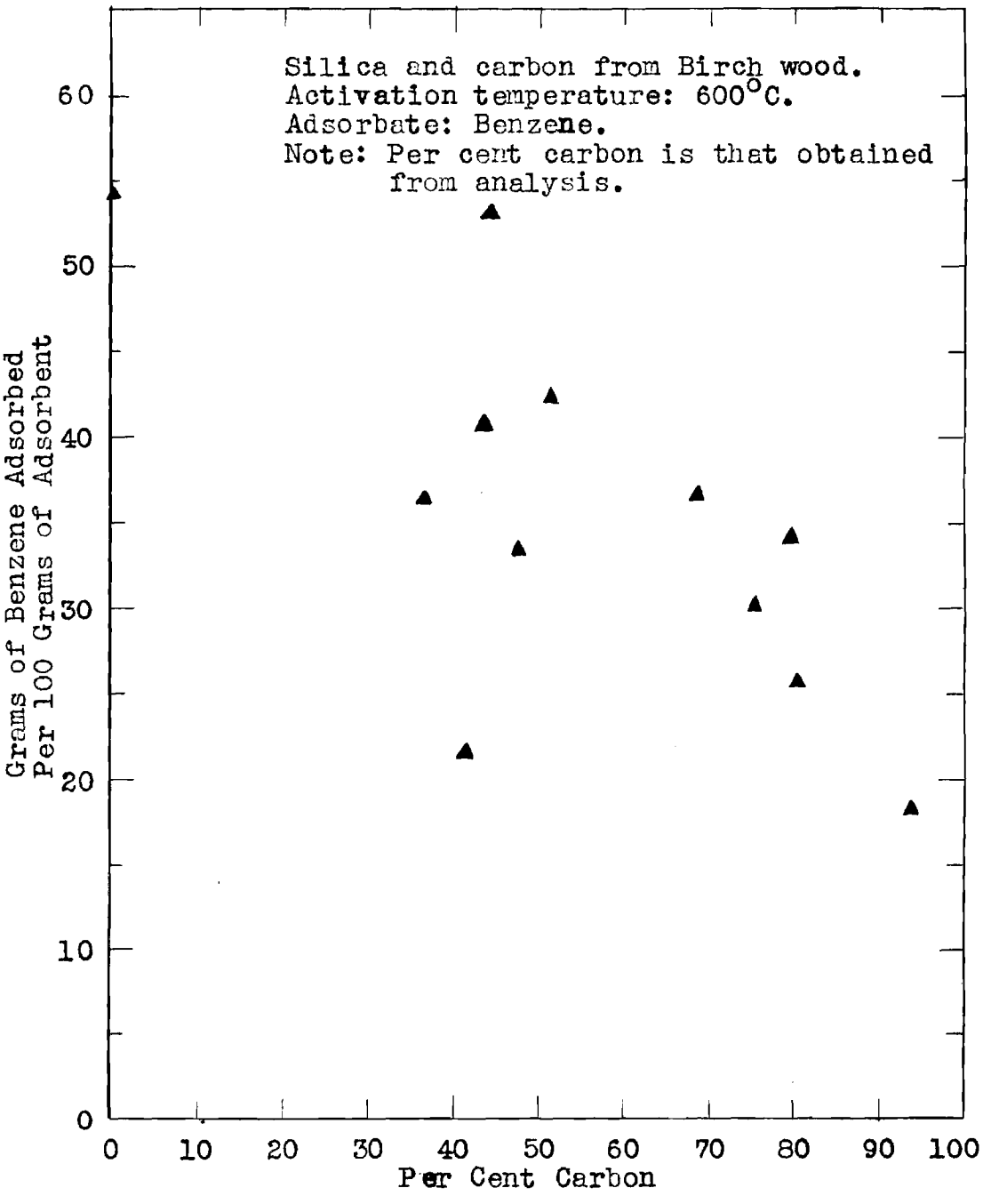

Figure 15

Effect of Carbon Content
on the Saturation Capacity for Benzene

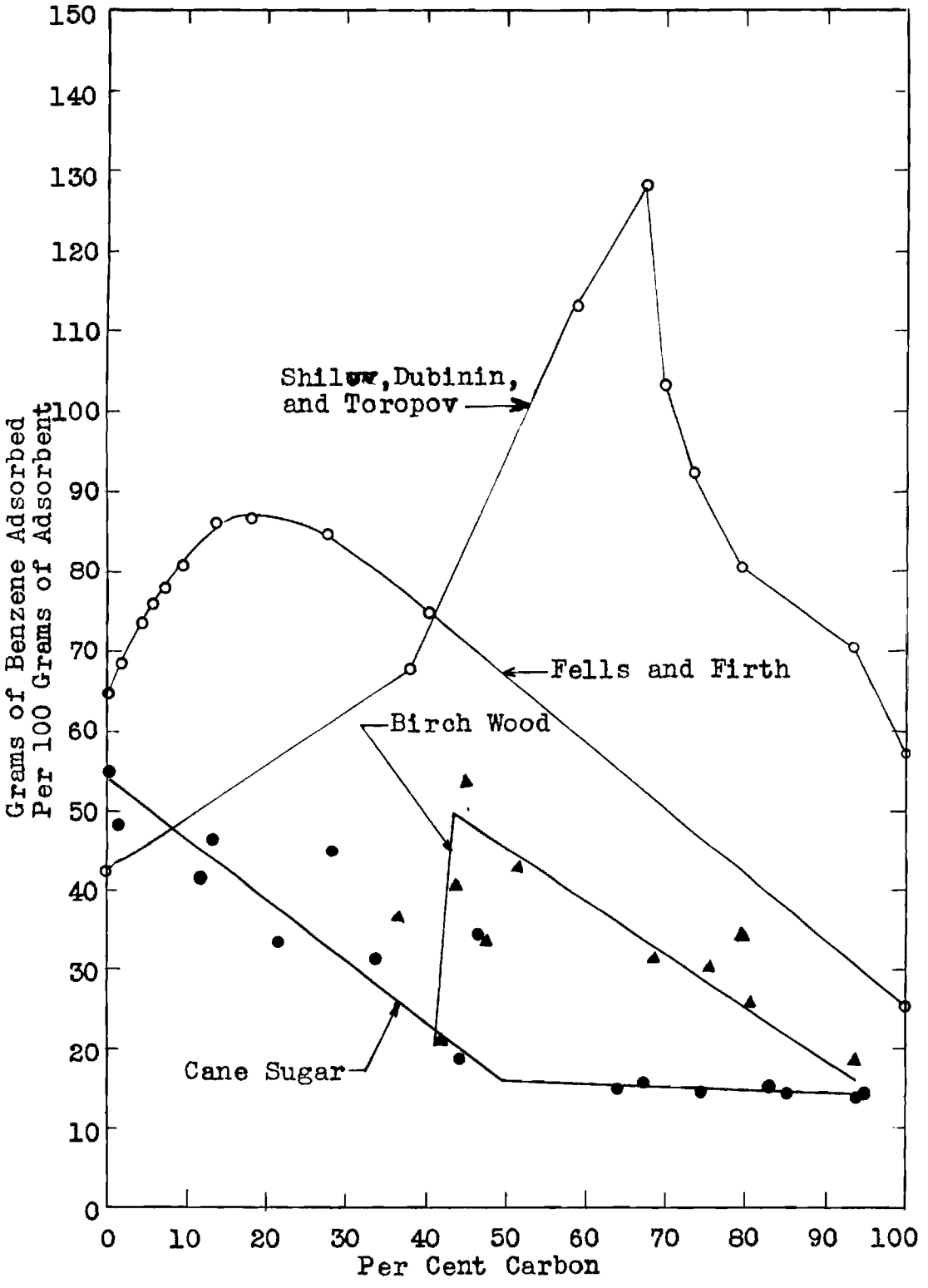

Figure 16

Benzene Adsorption Capacities of Adsorbents

No optimum composition resulting in maximum adsorption was found. It was because no peaks were found that the original purpose of this work was altered, since surface area measurements would not likely shed any light on the results obtained.

The following discussion will be based on the assumption that no maxima should exist, but that the materials should adsorb in proportion to the amount of each present. This is in agreement with the work of Lachs, but is contrary to the findings of Fells and Firth, and of Shilov, Dubinin, and Toropov.

On drawing a straight line connecting the amount of benzene adsorbed on silica gel and charcoal, one sees that with the samples prepared from silica and carbon from cane sugar, only one sample (9-A) shows adsorption in excess of that which would have been predicted.

An explanation for this can be found in the irregularities in the preparation of these samples. All three of the above samples were carbonized at temperatures reaching above 300°C; sample 9-A at a temperature reaching 360°C, sample 10-A at a temperature reaching 345°C, and sample 11-A at a temperature reaching 350°C. Samples 9-A and 10-A had also been washed with methyl alcohol in an attempt to speed the removal of organic degradation products formed during the carbonization of the sugar. Sample 10-A had also been activated at a temperature reaching 640°C. Otherwise, the conditions were the same as for the remaining adsorbents.

From these results it appears that washing process and the carbonization process are important steps in determining the activity of the adsorbents.

The small activity shown by the other samples, particularly the samples with high carbon content, could possibly be attributed to the fact some organic product formed during the carbonization of the sugar was not removed either during the carbonization or during the washing. This would have left the surface of the adsorbents covered with some fairly high molecular weight, water insoluble compounds. During activation these compounds would not be burned off because the process was carried out under vacuum.

In the light of the results obtained, it seems that the adsorbents should have been carbonized in open containers so that they would have been exposed to air. This would perhaps facilitate cleaning of the adsorbent surfaces by allowing any volatile organic products to escape easily and also further oxidation of any residues present. That activation of sugar charcoal in an atmosphere of oxygen resulted in charcoals superior to those obtained when the activation was carried out in nitrogen or helium was reported by McBain and Sessions.[4] While carbonization and activation are separate steps, any removal of products likely to cause

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[4] J. W. McBain and R. F. Sessions, J. Phys. Chem., 40, 611 (1936).

a decrease in capacity of the adsorbents in any step prior to activation should be helpful.[5]

With the results obtained with the adsorbents of mixtures of silica with birch wood, the majority of points fall above the line connecting the capacities of charcoal and silica gel when benzene was used as adsorbate, and approach this line when water was used as adsorbate.

For samples having greater than fifty per cent carbon, the capacities decrease directly with the carbon content and were as much as twenty per cent greater than for the adsorbents from sugar having the same percentage carbon.

Attention might be called to the fact that samples 1D-A and 11D-A were prepared with the same amounts and concentrations of reagents. The details of their preparations showed that sample 1D-A had not been filtered as free of the sodium silicate as had sample 11D-A. This meant that 1D-A contained proportionately more sodium silicate. The fact that 1D-A shows slightly less carbon on a percentage basis, and shows slightly greater capacity is in line with the above facts.

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[5]For a discussion of the activation of charcoals by oxidation of hydrocarbons on the adsorbent surfaces, see McBain, Sorption of Gases by Solids, p. 64; H. Briggs, Proc. Roy. Soc. (London), A, 1921, 100, 88; and H. N. Holmes, Introductory Colloid Chemistry (New York: John Wiley and Sons, Inc., 1934), p. 157.

Samples 10D-A, 11D-A, and 12D-A present an interesting problem since they differ by less than four per cent in their carbon content, yet show such wide variance in their capacities. An explanation can perhaps be found in the concentrations of the sodium silicate used in soaking the birch shavings.

The relationship between the saturation capacities of the adsorbents prepared from birch wood and the densities of the sodium silicate solutions used to soak the shavings is shown in Figure 17. From this Figure it is seen that maximum activity was obtained when a sodium silicate solution of density 1.10 was used. The cause for this was not studied, but it seems likely that sodium silicate solutions of density greater than 1.10 were not able to penetrate the shavings as easily as the more dilute solutions. When the zinc chloride was added to the samples which had been soaked in the more concentrated solutions of sodium silicate, the formation of a crust around the shavings was noticed. The zinc chloride might cause an inactive silica coating to be formed around the wood. The resulting adsorbent would then actually be a mechanical mixture rather than an intimate mixture of silica and charcoal.

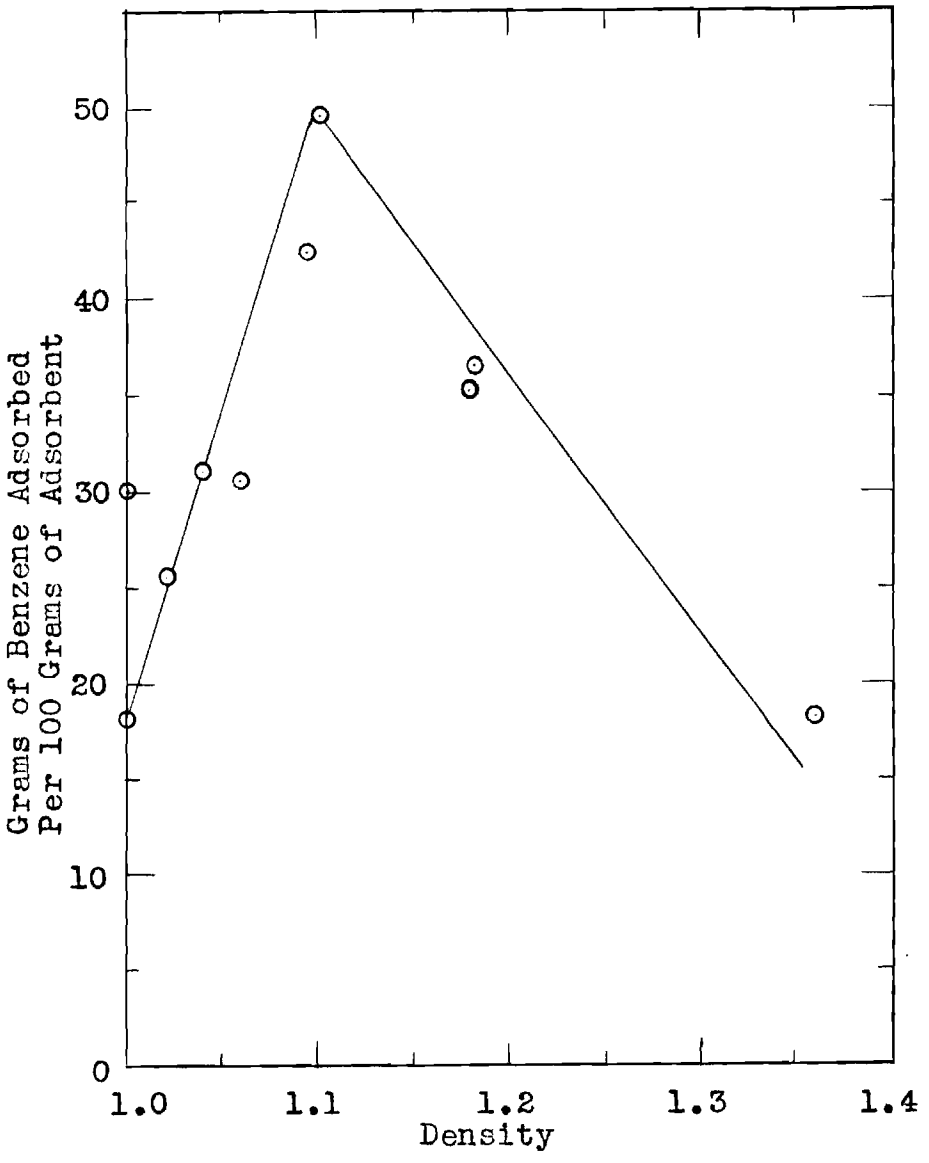

Figure 17

Effect of Density of Sodium Silicate Solution on the Capacities of the Adsorbents Prepared With Birch Wood

Comparison of the Amounts of Water and of Benzene Adsorbed

With the adsorbents prepared from silica and carbon from cane sugar, both benzene and water were adsorbed about the same, weight for weight (see Figure 18), although benzene was adsorbed slightly more on the high carbon samples. With the low carbon samples (0-25 per cent carbon) water was adsorbed to the greater extent, being as much as fourteen per cent more for straight silica gel.

With the series of adsorbents prepared by the use of birch wood, the weight of benzene adsorbed is greater in every case than the weight of water adsorbed on the same adsorbent. This is contrary to the work reported by Shilov, Dubinin, and Toropov, who found that water was adsorbed to the greater extent.

The fact that both water and benzene are adsorbed about the same, weight for weight, is not so strange since the molecular volume of water is 18 ml per mole and that of benzene is 89 ml per mole, about five times that of water. The molecular weight of benzene is a little over four times that of water. This means that for a given surface area to be covered, slightly less benzene would be required than water, weight for weight.

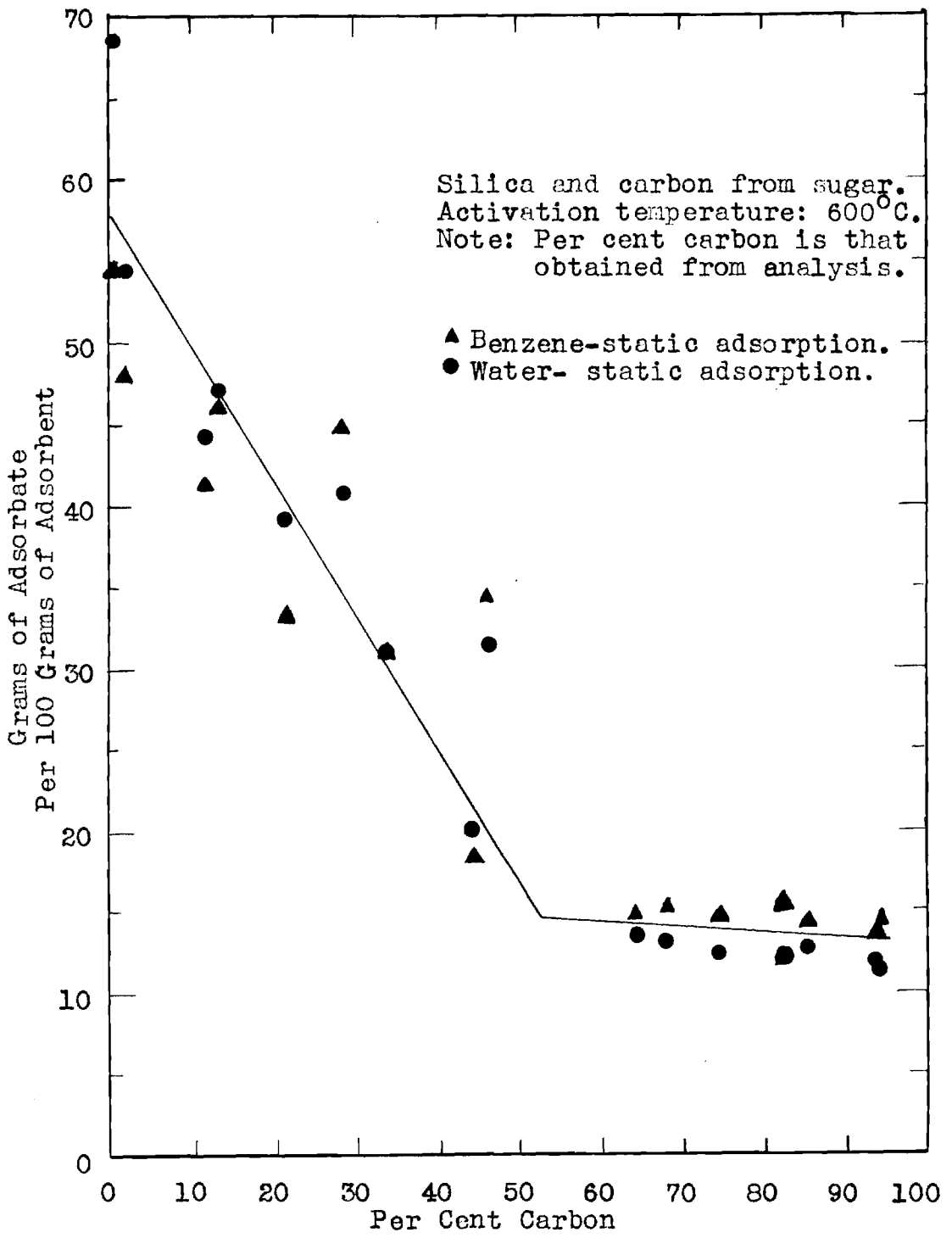

Figure 18

Comparison of Amounts of Benzene and Water Adsorbed

Effect of the Activation Temperature on the Activity

The adsorbents prepared from silica and carbon from cane sugar were activated at two temperatures — 300°C and 600°C — thereby enabling the effect of the activation temperature on the activity of the adsorbents to be investigated. It was known that sugar charcoal shows increased activity when activated in the neighborhood of 350 to 400°C and also when activated in the neighborhood of 920 to 960°C, with a minimum appearing at about 600°C.[6] Since the adsorbents prepared by Fells and Firth were activated at 600°C, the temperature of the minimum of activity of carbon, it was thought that possibly 300°C would be the most desirable temperature to use for the activation from both the standpoint of the charcoal and the silica. It has been reported by Bartel and Almy[7] that 300°C is the best temperature for activating silica gel. However, Patrick, Frazer, and Rush,[8] and also Holmes and Elder[9] report that the adsorption capacity of silica gel is not greatly decreased until a temperature above 800°C was reached.

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[6]McBain and Sessions, op. cit., p. 607.

[7]F. E. Bartel and E. G. Almy, J. Phys. Chem., 36, 489 (1932).

[8]W. A. Patrick, J. C. W. Frazer, and R. I. Rush, J. Phys. Chem., 31, 1511 (1927).

[9]H. N. Holmes and A. L. Elder, J. Phys. Chem., 35, 86 (1931).

CHAPTER VI

SUMMARY AND CONCLUSIONS

Summary.—Three series of intimately mixed adsorbents of silica and charcoal were prepared. Two of these were prepared identically from silica and cane sugar, but were activated at 300°C and 600°C respectively. The third series, prepared from silica and birch wood by using zinc chloride, was also activated at 600°C. These adsorbents were all analyzed for silica, carbon, water, and hydrogen. The saturation capacities for water were determined by the dynamic and by the static method. Break points were also determined using water as adsorbate. In addition, the static adsorption capacities for benzene were determined for the adsorbents that were activated at 600°C.

Conclusions.—From the results of the experimental work performed, the following conclusions have been drawn.

(1) The dynamic and the static methods for determining saturation capacities give essentially the same final saturation values with water, the only adsorbate that was investigated by the use of both methods.

(2) The dynamic method is the more rapid of the two, but it is also more laborious. However, the results more nearly approach those found in practical problems in industry.

(3) Of the two adsorbates, water and benzene, benzene is much more readily adsorbed during the first stages of adsorption. The relative activities of a series of adsorbents can be fairly safely predicted within two days when benzene is used as the adsorbate, and in about eight days when water is used.

(4) The adsorbents showing the greatest capacity for water show also the greatest capacity for benzene.

(5) Increasing the carbon content of the adsorbents generally decreases the rate of adsorption of the adsorbents for water.

(6) The water content of the analyzed samples increases directly with the carbon content and decreases with the temperature of activation.

(7) The hydrogen content of the adsorbents increases directly with the carbon content and increases with the temperature of activation.

(8) With adsorbents prepared from mixtures of silica and carbon from cane sugar, the silica shows little effect on the adsorptive capacity after the carbon content reaches about fifty per cent. Between 50 and 100 per cent carbon, the capacity is essentially the same as sugar charcoal. From 0 to 50 per cent carbon the adsorptive capacity increases steadily to that of silica gel.

(9) With mixed adsorbents of silica and carbon from birch wood prepared using zinc chloride solution, the

adsorption capacity increases directly with the silica content until about 45 per cent carbon is reached. The capacity then drops off sharply as the silica content increases further. No samples having carbon content lower than about 35 per cent can be prepared by the method that has been used.

(10) The mixed adsorbents from silica and carbon from cane sugar show about the same capacity when activated at 300°C as they do when activated at 600°C.

(11) The break point capacities do not parallel the saturation capacities of the adsorbents, e.g., an adsorbent having a comparatively high capacity at saturation does not necessarily have a high break point capacity (see Figure 19).

(12) The break point capacities show a minimum between forty and fifty per cent carbon for all series of mixed adsorbents investigated.

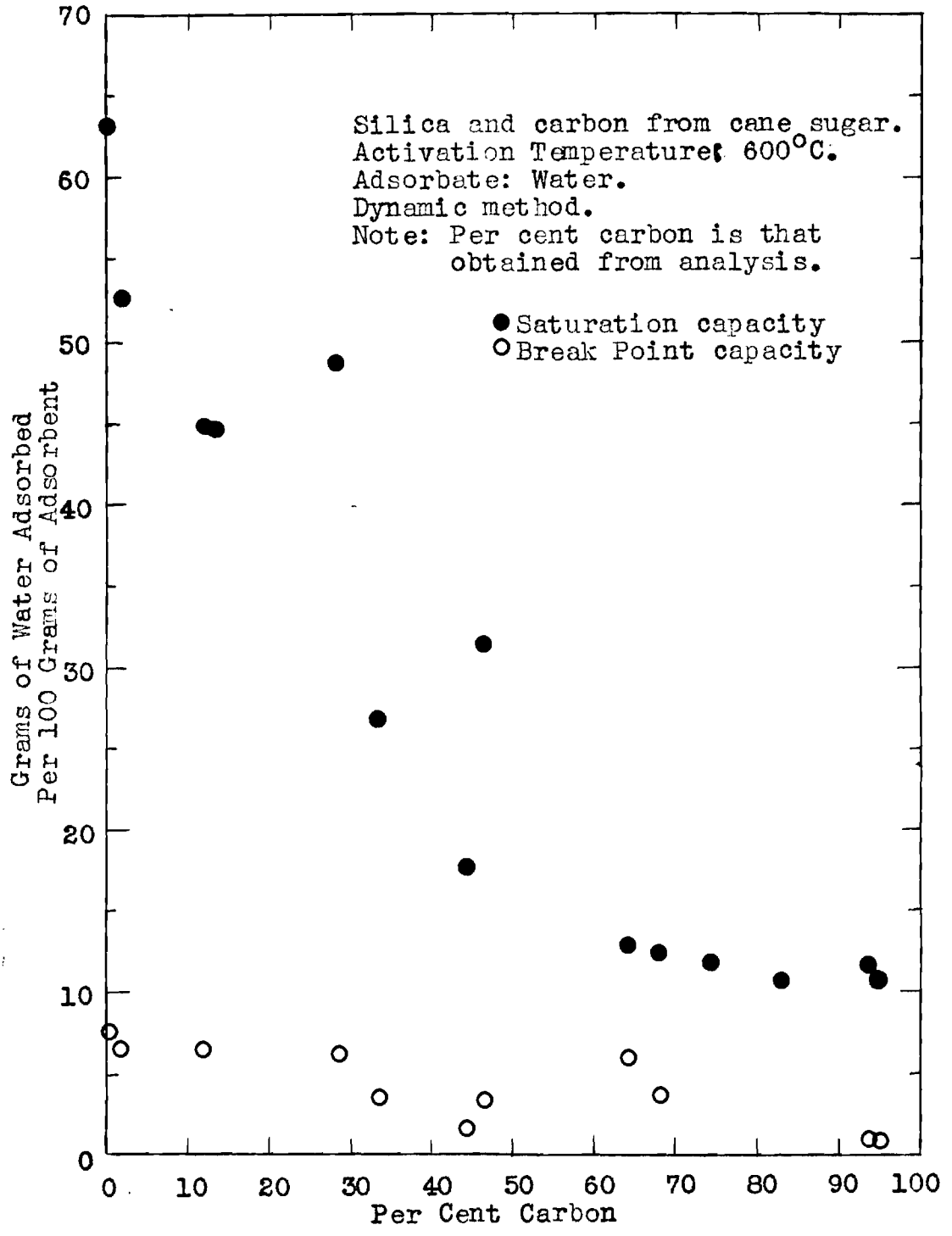

Figure 19

Saturation and Break Point Capacities

CHAPTER VII

RECOMMENDATIONS

Since no peaks were found, the results of this work fail to confirm the work of either Fells and Firth, or of Shilov, Dubinin, and Toropov. Since the details of the experimental procedure reported by these authors was not given in too complete detail, it might be well to vary the procedure that was used in preparing the adsorbents investigated in this thesis in an attempt to obtain activities comparable with those of the above mentioned investigators.

Also, it might be well to investigate the systems which Chowdhury, et al., have reported as showing optimum activity and see if the maxima found by them exist, or if they were due to some fortuitous treatment of the mixed adsorbents.

APPENDIX

Table 1-A

Summary of the Preparation of Mixed Adsorbents from Sodium Silicate and Cane Sugar

Sample number	Materials used: Volume sodium silicate[1] (ml)	Volume hydrochloric[2] acid (ml)	Weight cane sugar (grams)	Mixing temperature: Sodium silicate	Hydrochloric acid	Setting time[3] (hours)
1	100	100	---	50	50	2-4
2	100	100	---	50	50	2-4
3	100	100	---	50	50	2-4
4	100	100	---	50	50	1.5-12
5	100	100	---	45	45	1.5-2.7
6	100	100	---	60	60	1.0-2.3
7	100	100	---	45	45	1.5-2.0
8	100	100	---	55	55	1.2-1.4
9	100	100	50	33	33	0.5-18.3
10	100	100	25	33	33	1.0-4.2
11	100	100	75	32	32	2-4
12	100	100	100	27	27	2.5-6
13	100	100	50	30(?)	30(?)	2.2-4.2
14	100	100	150	30(?)	30(?)	5.7-7.6
15	100	100	---	0	0	3-4
16	100	100	200	2	7	4.4-7.1
17	100	100	250	12	3	6-14
18	---	100	400	--	--	---
19	200	200	2	3	3	3.9-5.3
21	200	200	40	3	3	3.6-4.2
22	75	75	300[a]	1	6	---
23	20	20	300[b]	25	25	---
24	200	200	20[b]	1	1	4.1-5.5
25	---	---	300[b]	--	--	---

[1]The specific gravity of the sodium silicate was 1.183 for samples 1-17, and 1.181 for samples 19-24.

[2]The specific gravity of the hydrochloric acid was 1.051.

[3]The solutions set sometime within the interval indicated.

[a]The sugar was first dissolved in 200 ml of water.

[b]The sugar was first dissolved in 300 ml of water.

Table 1-A (continued)

Summary of the Preparation of Mixed Adsorbents from Sodium Silicate and Cane Sugar

Sample number	First drying		Carbonization		Second drying	
	Time (hours)	Temperature range[4]	Time (hours)	Temperature range[5]	Time (hours)	Temperature range[4]
1	26.5	75-110	---	---	2.7	110-115
2	26.5	75-110	---	---	2.7	110-115
3	26.5	75-110	---	---	3	98-106
4	3.5	80-110	4.0	300-350	2.0	110
5	4.0	85-117	2.0	300-350	13	110
6	4.0	80-110	2.7	300-350	16	110-113
7	20	85-110	---	---	8.2	115
8	20	85-110	---	---	21.3	115
9	18	85-110	2.0	300-360	1.5	105
10	24	85-113	4.0	275-345	2.0	110
11	23.6	85-110	1.9	300-350	6.0	110-120
12	9.0	110-126	2.2	300-375	3.2	115-104
13	4.2	95-120	3.0	290-300	3.5	111
14	3.0	110-112	2.0	300	2.2	110-115
15	3.0	110-112	2.0	300	2.1	110
16	6.5	103-125	1.7	275-300	26.5	110
17	6.5	106	2.0	200-310	3.3	110-122
18	3.3	120	2	300-330	3.3	110-122
19	74.7	110-115	2	300	4.5	105-108
21	12.0	110-114	2.0	300	17.2	104-106
22	45.5	87- 92	2.0	300	17.6	106
23	19.7	105	2.0	290-300	3.2	105-110
24	18.1	106-115	2.0	300	14.0	120
25	46.5	95-117	2.0	305-320	16.2	117

[4]Indicates minimum and maximum temperatures. The average temperature was about 110°C.

[5]Indicates minimum and maximum temperatures. The average temperature was about 300°C.

Table 1-B

Summary of the Preparations of Mixed Adsorbents from Sodium Silicate and Birch Wood

Sample number	Materials used				
	Weight dry birch shavings (gm)	Volume sodium silicate (ml)	Specific gravity sodium silicate	Volume water (ml)	Volume zinc chloride (ml)
1D	25	400	1.181	---	45[a]
2D	25	200	1.195	200	86
3D	25	50	1.195	350	87
4D	25	10	1.191	390	86
5D	25	---	-----	400	44[a]
6D	25	300	1.195	100	87
7D[b]	--	---	-----	---	--
8D	25	100	1.195	300	86
10D	25	400	1.362	---	86
11D	25	400	1.181	---	86
12D	25	250	1.181	150	86
13D	25	150	1.181	250	86

[a]Only half of the sample was used.

[b]This is the remaining half of sample 5D.

Table 1-B (continued)

Summary of the Preparations of Mixed Adsorbents from Sodium Silicate and Birch Wood

Sample number	First heating Maximum temperature	Second heating Time (hours)	Second heating Temperature range[1]	Drying Time (hours)	Drying Temperature range[1]
1D	290	6.0	200-300	17	105
2D	215	7.2	to 300	11.0	106
3D	168	7.0	to 300	14.0	106
4D	168	7.1	175-300	7.6	110-115
5D	155	5.7	200-305	13.8	111
6D	200	7.0	to 300	15.5	112-110
7D	165	7.0	to 300	16.0	111-106
8D	210	6.8	to 310	12 to 24	120
10D	230	7.6	to 300	>24	110
11D	280	7.0	to 300	10.7	108-115
12D	178	7.0	to 325	20.0	108-119
13D	185	7.0	to 350	15.4	115

[1]The temperature range gives the maximum and minimum temperatures observed.

Table 2

Summary of the Activating Conditions

Sample number	Activating conditions		
	Time (hours)	Temperature range[1]	Pressure[2] (mm)
9-A	2	580-615	19
10-A	2.1	590-640	18
11-A	2.0	590-600	18
12-A	2.0	570-600	28
13-A	2.0	590-625	24
14-A	2.0	540-600	42
15-A	2.0	550-600	19
16-A	2.0	550-600	28
17-A	2.1	530-600	19
18-A	3.0	540-600	247
19-A	2.3	600-605	19
21-A	2.0	580-605	19
22-A	2.6	580-590	20
23-A	2.0	550-600	24
24-A	2.0	600	31
25-A	2.0	600-605	43
1-0	2.0	300-325	33
2-0	1.8	300-350	36
3-0	2.1	325-360	25
4-0	2.0	265-300	40
5-0	2.0	300-350	42
6-0	1	300-315	40
9-0	2.0	300-325	17
10-0	2.0	250-340	16
11-0	2.0	300	18
12-0	2.0	225-310	40
13-0	2.0	275-305	28
14-0	2.0	300-310	37
16-0	2.0	290-340	19
17-0	2.1	300	32
18-0	2.0	300	38

[1]Minimum and maximum temperature.

[2]Pressure at the end of activation.

Table 2 (continued)

Summary of the Activating Conditions

Sample number	Activating conditions		
	Time (hours)	Temperature range[1]	Pressure[2] (mm)
1D-A	2.0	580-600	44
2D-A	2.0	600-625	44
3D-A	2.0	590-600	59
4D-A	2.0	580-600	30
5D-A	2.1	590-600	45
6D-A	2.0	600-605	43
8D-A	2.0	590-600	35
10D-A	2.0	600	53
11D-A	2.0	580-640	35
12D-A	2.0	550-600	27
13D-A	2.0	550-625	32

[1]Minimum and maximum temperature observed.

[2]Pressure at the end of activation.

Table 3

Composition of the Adsorbents

Sample number	Percentage from analysis			Corrected percentage				Ratio of Silica to carbon	
	Silica	Carbon	Water	Silica	Carbon	Water	Hydrogen	Silica	Carbon
9-A	67.6	28.3	10.3	67.6	28.3	3.3	0.8	70.5	29.5
10-A	85.4	13.3	4.2	85.4	13.3	1.0	0.3	86.5	13.5
11-A	49.9	46.2	14.6	49.9	46.2	2.6	1.3	52.0	48.0
12-A	63.0	33.7	9.9	63.0	33.7	2.5	0.7	65.1	34.9
13-A	51.3	44.1	13.6	51.3	44.1	3.5	1.1	53.7	46.3
14-A	30.1	64.0	1.9	30.1	64.0	1.9	---	32.0	68.0
15-A	98.4	0.3	1.8	98.4	0.3	1.3	0.1	99.6	0.4
16-A	23.7	67.8	19.9	23.7	67.8	7.1	1.4	25.9	74.1
17-A	19.4	74.2	20.5	19.4	74.2	4.6	1.8	20.7	79.3
18-A	0.0	93.8	2.5	0.0	93.8	2.5	---	0.0	100.0
19-A	97.4	1.9	6.7	97.4	1.9	0.0	0.7	98.1	1.9
21-A	76.4	21.5	6.7	76.4	21.5	1.5	0.6	78.0	22.0
22-A	12.0	82.9	18.4	12.0	82.9	3.5	1.7	12.6	87.4
23-A	3.2	85.3	24.9	3.2	85.3	9.8	1.7	3.6	96.4
24-A	87.2	11.9	7.6	87.2	11.9	0.8	0.1	88.0	12.0
25-A	0.0	94.8	25.6	0.0	94.8	2.7	2.6	0.0	100.0

Table 3 (continued)

Composition of the Adsorbents

Sample number	Percentage from analysis			Corrected percentage				Ratio of silica to carbon	
	Silica	Carbon	Water	Silica	Carbon	Water	Hydrogen	Silica	Carbon
3-0	95.3	0.0	4.7	95.3	0.0	4.7	0.0	100.0	0.0
4-0	94.1	0.4	5.6	94.1	0.4	5.5	0.0	99.5	0.5
5-0	97.5	0.0	2.4	97.5	0.0	2.5	0.0	100.0	0.0
9-0	58.3	27.5	15.9	58.3	27.5	14.0	0.2	68.0	32.0
10-0	76.3	15.9	11.7	76.3	15.9	7.3	0.5	82.8	17.2
11-0	39.9	40.0	22.1	39.9	40.0	19.9	0.3	50.0	50.0
12-0	38.9	48.8	17.8	38.9	48.8	11.6	0.7	44.4	55.6
13-0	39.3	40.4	21.0	39.3	40.4	20.2	0.1	49.3	50.7
14-0	21.1	55.4	26.9	21.1	55.4	23.1	0.4	27.6	72.4
16-0	17.7	61.2	25.9	17.7	61.2	20.5	0.6	22.4	77.6
18-0	0.0	63.3	31.9	0.0	63.3	31.9	0.0	0.0	100.0

Table 3 (continued)

Composition of the Adsorbents

Sample number	Percentage from analysis			Corrected percentage				Ratio of silica to carbon	
	Silica	Carbon	Water	Silica	Carbon	Water	Hydrogen	Silica	Carbon
1D-A	60.2	36.6	21.8	60.2	36.6	0.9	2.3	62.2	37.8
2D-A	44.1	51.5	14.9	44.1	51.5	3.1	1.3	46.2	53.8
3D-A	11.0	80.2	20.4	11.0	80.2	7.4	1.4	12.0	88.0
4D-A	16.8	75.5	16.2	16.8	75.5	6.7	1.1	18.2	81.8
5D-A	0.0	93.3	26.6	0.0	93.3	4.2	2.5	0.0	100.0
6D-A	48.0	47.6	12.8	48.0	47.6	3.3	1.1	50.2	49.8
8D-A	17.9	68.6	14.3	17.9	68.6	13.4	0.1	20.7	79.3
10D-A	49.6	41.7	9.5	49.6	41.7	8.6	0.1	54.4	45.6
11D-A	50.0	43.4	13.6	50.0	43.4	5.7	0.9	53.6	46.4
12D-A	49.8	44.4	11.5	49.8	44.4	5.1	0.7	52.8	47.2
13D-A	13.8	79.2	19.3	13.8	79.2	5.4	1.5	14.8	85.2

Table 4

Adsorption Capacities of the Adsorbents for Water and Benzene

Sample number	Grams of adsorbate per 100 grams of adsorbent at saturation		
	Water		Benzene
	(Dynamic)	(Static)	(Static)
9-A	48.7	41.0	44.9
10-A	44.6	47.2	46.1
11-A	31.5	31.6	34.5
12-A	27.0	31.4	32.2
13-A	17.8	20.1	19.0
14-A	13.0	13.8	14.9
15-A	63.1	68.9	54.8
16-A	12.5	13.0	15.1
17-A	12.0	12.3	14.6
18-A	12.0	11.8	13.6
19-A	52.9	54.5	48.1
21-A	----	39.0	33.2
22-A	10.6	11.9	15.1
23-A	----	12.7	14.3
24-A	44.9	44.1	41.2
25-A	10.9	11.2	14.3
1-0	58.4	----	----
2-0	64.5	----	----
3-0	53	60.0	----
4-0	59.3	62.0	----
5-0	----	64.0	----
6-0	66.0	71.0	----
9-0	44.0	47.0	----
10-0	48.0	47.7	----
11-0	28.8	30.0	----
12-0	26.7	28.9	----
13-0	20.4	24.6	----
14-0	10.0	12.4	----
16-0	10.0	10.8	----
18-0	----	9.1	----

Table 4 (continued)

Adsorption Capacities of the Adsorbents for Water and Benzene

Sample number	Grams of adsorbate per 100 grams of adsorbent at saturation		
	Water		Benzene
	(Dynamic)	(Static)	(Static)
1D-A	26.8	31.0	36.4
2D-A	34.5	39.2	42.4
3D-A	19.7	22.7	25.6
4D-A	25.4	23.9	30.1
5D-A	----	15.7	18.3
6D-A	26.2	30.8	33.4
8D-A	25.3	33.0	36.7
10D-A	13.6		21.5
11D-A	28.5	41.5	40.7
12D-A	34.4	43.5	53.1
13D-A	----	25.5	34.4

Table 5

Results of the Break Point Determinations

Sample number	Per cent adsorbed by weight	Flow rate (ml/min)	Sample weight (gm)
9-A	6.16	108	3.9025
11-A	3.39	80	5.2586
12-A	3.48	70	3.6769
13-A	1.57	80	4.4992
14-A	5.94[a]	100	10.0331
15-A	7.51	100	6.9716
16-A	3.50	94	9.8553
18-A	0.81	100	3.5874
19-A	6.42	90	5.6918
22-A	1.16	80	4.8795
24-A	6.34	100	3.7321
25-A	0.39	100	2.2933
4-0	3.92	150	4.31
9-0	6.73	108	4.8908
10-0	9.71	64	4.6835
11-0	5.70	70	5.3710
12-0	4.67	---	7.06
13-0	5.03	---	7.74
14-0	6.56	110	7.6999
16-0	4.25	120	11.1150
18-0	0.00	---	3.8114
1D-A	4.64	105	2.6034
2D-A	1.26	104	2.4424
4D-A	5.76	88	1.5282
6D-A	0.51	92	2.0466
8D-A	0.53	90	1.6649
10D-A	0.39	70	1.5690
11D-A	3.04	90	1.8491
12D-A	1.33	100	1.3720

[a]The break point had not been reached.

Table 6

Summary of the Results
of the Work of Fells and Firth[1]

Percentage composition			Grams adsorbed per 100 grams of adsorbent	
Silica	Carbon	Water	Benzene	Toluene
93.20	------	6.80	65.4	63.3
91.65	1.94	6.41	68.1	65.4
88.37	4.61	7.02	73.2	60.5
86.96	5.93	7.11	75.6	70.8
86.12	7.28	6.60	77.8	72.8
83.76	9.60	6.64	80.2	75.6
79.56	13.52	6.92	85.9	80.1
75.59	18.10	6.31	86.2	82.7
66.59	27.41	6.00	84.3	73.9
53.96	40.20	6.84	74.8	67.7
-----	100.00	----	25.1	22.3

[1]H. H. Fells and J. B. Firth, J. Soc. Chem. Ind., 41, 40T (1927).

Table 7

Summary of the Results
of the Work of Shilov, Dubinin, and Toropov[1]

Percentage composition		Grams adsorbed per 100 grams of adsorbent	
Silica	Carbon	Water	Benzene
100	-----	54.47	42.20
52.99	37.99	109.00	67.63
38.13	58.93	121.20	113.10
28.45	67.65	140.60	128.00
25.89	69.87	113.50	103.10
25.61	73.29	100.51	92.10
18.76	79.61	------	80.08
2.90	93.71	105.86	70.69
-----	100	71.33	57.02

[1]Von N. Shilov, M. Dubinin, and S. Toropov, Kolloid Z., 49, 120 (1929).

CORRECTION OF THE RESULTS OF THE ANALYSES

In most of the analyses of the samples of intimate mixtures of carbon and silica gel the total per cent of material found based on the assumption that only silica, carbon, and water were present in the sample was found to be high, being as high as 119 per cent of the theorectical. In these analyses the per cent water was determined by the gain in weight of the tube containing calcium chloride and was found to be as high as 28 per cent of the sample. It was thought that these high results might be due to the combustion of hydrogen in the sample. This hydrogen could conceivably be present either as adsorbed hydrogen or as part of some high molecular weight organic compound which might have been formed during the preparation of the adsorbents. The method used to correct for this apparent error is outlined below.

The assumption was made that the samples consisted only of silica, carbon, water, and hydrogen.

Let W_s be the weight of the sample,

W_{SiO_2} be the weight of the residue after combustion,

W_C be the weight of the carbon in the sample,

W_{H_2O} be the weight of the water present in the sample as adsorbed water,

W_H be the weight of the hydrogen present in the sample.

Therefore $$W_s = W_{SiO_2} + W_C + W_{H_2O} + W_H. \quad (1)$$

Rearranging $$W_s - W_{SiO_2} - W_C = W_H + W_{H_2O} \quad (2)$$

Letting $W_{H_2O\ total}$ be the weight of the water as determined by the gain in weight of the tube containing calcium chloride, and $W^*_{H_2O}$ be the weight of the water formed from the combustion of the hydrogen, we obtain

$$W_{H_2O,\ total} = W_{H_2O} + W^*_{H_2O} \quad (3)$$

Subtracting (3) from (2) we obtain

$$W_s - W_{SiO_2} - W_C - W_{H_2O,\ total} = W_H - W^*_{H_2O} \quad (4)$$

The equation for the reaction of hydrogen with oxygen to form water is

$$H_2 + 1/2\ O_2 \longrightarrow H_2O. \quad (5)$$

Knowing the molecular weights (hydrogen, 2.016; oxygen, 32.00; water, 18.02) the following ratio can be obtained:

$$\frac{W_H}{2.016} = \frac{W^*_{H_2O}}{18.02} \quad (6)$$

from which we obtain

$$W^*_{H_2O} = 8.96 \times W_H \quad (7)$$

Substituting (7) in (4) and collecting and rearranging terms we obtain

$$W_H = \frac{W_{SiO_2} + W_C + W_{H_2O,total} - W_s}{7.96} . \qquad (8)$$

From equation (7) the weight of water formed from the combustion of this hydrogen can be found, then from equation (3), W_{H_2O} can be found.

SENSITIVITY OF THE BREAK POINT INDICATOR

In order to get some indication of the sensitivity of the break point indicator, two break point determinations using two portions of the same sample of silica gel were made. A U-tube filled with calcium chloride was attached after the break point indicator to catch any water vapor that was passed by the adsorbent before the indicator responded. The U-tube was weighed before and after the break point determination. The results are given below.

Run number	1	2
Weight of the silica gel	4.6789 gm	9.3910 gm
Flow rate	100 ml/min	100 ml/min
Total time of run before break point indicator responded	44 min	117 min
Total time of run	49 min	117 min
Grams of water adsorbed by the silica gel	0.1679gm	0.4513gm
Grams of water absorbed by the calcium chloride U-tube	0.0060gm	0.0082gm
Per cent of water passed by the silica gel	3.71	1.79
Approximate rate of decrease of the resistance of the break point indicator at the time of the detection of the break point (ohm/min)	500,000	900,000

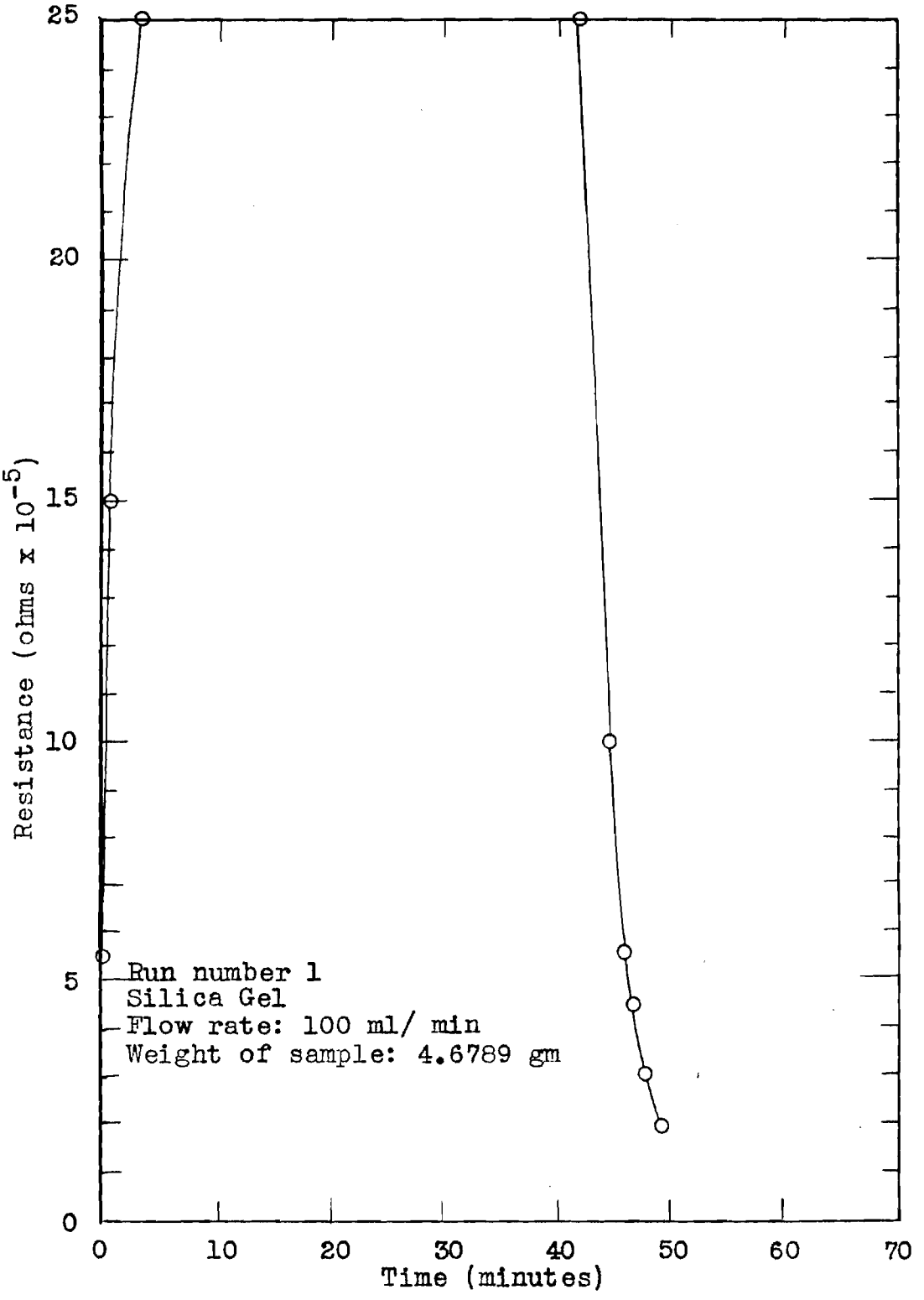

Figure 20

Resistance of Break Point Indicator

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